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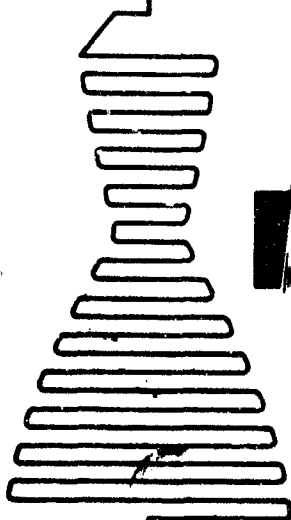
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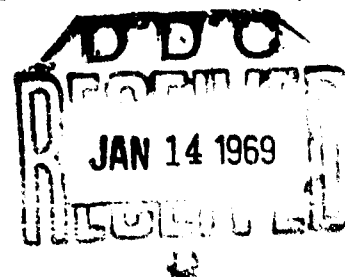
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ROCKETDYNE

A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION
6633 CANOGA AVENUE, CANOGA PARK, CALIFORNIA 91304

R-7723

(Unclassified Title)

SEMIANNUAL REPORT,
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FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Navy Contract Nonr 4428(00) and covers the period 30 May 1968 through 30 November 1968. The program manager was Dr. E. A. Lawton, Manager, Synthetic and Propellant Chemistry. The work was conducted in Oxidizer and Fluorine Chemistry with Dr. D. Pilipovich, Principal Scientist as the responsible scientist. Staff members contributing to the technical effort were Dr. D. Pilipovich, Dr. C. J. Schack, Dr. K. O. Christie, Mr. R. D. Wilson, and Dr. W. Maya.

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ABSTRACT

Glow discharge fluorinations, using a solid reactant-activated fluorine technique, were conducted with ClF_3O , FClO_2 , and FClO_3 . The preferred course of the reaction resulted in the formation of ClF_5 through oxygen displacement. Ultraviolet activated fluorination reactions yielded ClF_3O from the system $\text{IOF}_5\text{-ClF}$ but did not give bromine oxyfluorides from the system $\text{BrF}_5\text{-O}_2$. Neither glow discharge nor uv activation of fluorine resulted in the fluorination of BrF_5 to BrF_7 .

High-pressure and high-temperature fluorination of $\text{ClF}_2^+\text{AsF}_6^-$ and $\text{ClO}_2^+\text{AsF}_6^-$ was investigated as a route to higher valent chlorine oxyfluoride cations but no reaction occurred. Similar conditions did not produce the unknown chlorine oxyfluoride, ClF_5O , when RbClF_4O or CsClF_4O were fluorinated. The preparation of ClF_3O from the new hypochlorite, SF_5OCl , as a substrate was unsuccessful.

Efforts were made to synthesize new oxidizing cations by the interaction of fluorine and a precursor in the presence of a strong Lewis acid. Reactions of ClF_5 , F_2 and the acids BF_3 , AsF_5 , and SbF_5 were directed toward the preparation of ClF_6^+ . However, the chlorine fluoride salts isolated contained only ClF_2^+ and ClF_4^+ . Bromine pentafluoride, F_2 , and SbF_5 gave $\text{BrF}_5 \cdot 2\text{SbF}_5$ and no BrF_6^+ . The identity of the BrF_5 complex was proven by an independent synthesis. The synthesis of the cations ClF_4O^+ , ArF^+ and OF_3^+ from ClF_3O , Ar or OF_2 in conjunction with F_2 and SbF_5 was not realized. A by product of one of these reactions, $\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$, furnished useful spectral data for the $\text{Sb}_2\text{F}_{11}^-$ anion whose previous characterization was somewhat uncertain.

The structural investigation of ClF_3O was completed by obtaining the Raman spectrum of the liquid which conclusively proved the earlier suggested C_s symmetry for the molecule. The

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vibrational spectra of ClF_2O^+ showed it to be of C_s symmetry while the spectra of ClF_4O^- proved its symmetry to be C_{4v} . The Raman spectrum of solid $\text{ClO}_2^+\text{AsF}_6^-$ confirmed the previously postulated C_{2v} structure.

Dissociation pressure-temperature data were measured for $\text{ClO}_2^+\text{BF}_4^-$ and the desired thermodynamic values were calculated. Data correlation allowed an order of increasing Lewis base strength to be established as: $\text{ClF}_5 \approx \text{ClF} < \text{ClF}_3 < \text{FCIO}_2 < \text{ClF}_3\text{O}$.

The preparation of " IOF_3 " was not quantitatively achieved from I_2O_5 and IF_5 as reported in the literature. Modified reaction conditions gave FIO_2 which was also formed by pyrolysis of " IOF_3 ". Infrared and analytical data for iodyl fluoride are presented. Preliminary efforts to form IO_2^+ salts from FIO_2 and Lewis acids were only partially successful. Reaction of iodyl fluoride and FNO indicated a facile fluorination occurred but accompanied by oxygen abstraction from the iodine species.

Oxidative chlorofluorinations were investigated using ClF with SOF_2 and SO_2 . Thionyl fluoride reacted to give only SOF_4 and Cl_2 under a variety of conditions. The excellent conversions found make this the first practical synthetic route to SOF_4 not involving elementary fluorine. Sulfur dioxide was quantitatively converted to ClSO_2F by the action of ClF .

The preparation and characterization of complexes containing the NF_2O^+ cation are described in a manuscript, Appendix A.

(Confidential Abstract)

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INTRODUCTION

The general direction of this program continues to be oriented toward halogen fluoride chemistry. The previous report (Ref. 3) properly introduces a number of study areas that were more fully explored recently. Specifically, the reaction chemistry of ClF_3O , as well as a more definitive structural evaluation of its derivatives, was pursued further.

Our fluorination studies during the report period were directed at higher energy species. The approaches in this connection utilized glow discharge, uv activation and Lewis acid catalysis.

Two minor studies were carried out. One of these, a continuation of earlier work, is aimed at a more complete elucidation of properties of sketchily reported compounds such as IOF_3 , FIO_2 , etc., as well as a definition of the reaction chemistry. In addition, the interesting reaction chemistry of ClF is being further developed, again as a logical extension of previously reported work.

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DISCUSSION

FLUORINATION STUDIES

Glow Discharge Reactions

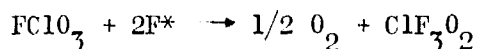
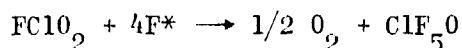
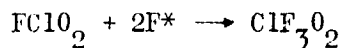
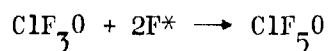
Fluorination reactions, in which glow discharge activation of elemental fluorine serves as the reaction stimulus, are generally quite uncontrolled. For example, if the substrates are reacted at a temperature at which they have some volatility, the overall fluorination process proceeds through atomization of the substrate, followed by random recombination reactions involving some fluorination. Recognition of this problem led to modification of the discharge method. This entailed lowering the reaction temperature to "freeze out" the substrate reactant making it an immobile, solid wall. A convenient temperature for most inorganic oxidizers is that obtained from liquid nitrogen cooling, -196°C . This modification results in a fluorination process wherein reaction is achieved by the impingement of activated fluorine on the solid wall. The cold wall provides a means for the removal of excess energy and aids in stabilizing the products formed.

Employing these techniques, the fluorination of some Cl-O compounds (Cl_2O and FClO_2) was examined some time ago (Ref. 1). It was found that fluorination of these compounds did occur to give limited yields of ClF_5 . However, the reaction was very inefficient in terms of fluorine utilization and somewhat inconsistent as to product formation. To overcome this inefficiency, the method was further altered to incorporate an all-glass, gas-circulating pump. In this manner, fluorine could be passed through the discharge and reaction zones, and the unreacted portion (the bulk of the fluorine) recycled until consumed. This apparatus, when used for the fluorination of Cl_2O , gave much improved results; a 45 percent conversion to ClF_5 and for the first time a detectable yield of Florox, 1 to 2 percent (Ref. 2).

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An investigation of the fluorination of chlorine oxyfluorides via this technique has now been completed. These experiments were aimed at the formation of new, covalent chlorine oxyfluorides, specifically ClF_5O and ClF_3O_2 . All the known, covalent Cl-F-O compounds, except FOClO_3 , were used as substrates. The types of reactions sought are:



The conditions of the experiments and the results are summarized in Table 9, page 30. Very good chlorine material balances were obtained in these reactions, but a fluorine balance was not possible due to appreciable O_2F_2 formation and its subsequent decomposition during workup.

Overall, it was found that no new chlorine oxyfluorides were formed. Extensive fluorination of Cl-O bonds did take place, generally the replacement of one oxygen atom by two fluorine atoms. Keeping conditions of the reactions essentially constant it was noted that the yield of fluorinated products was dependent on the operating fluorine pressure during the glow discharge. Higher pressures produced higher yields of fluorinated products.

With all the substrates examined, it was observed that chlorine pentafluoride was the preferred product. As a product of ClF_3O or FClO_2 , this represents a simple substitution of oxygen by fluorine with no change in oxidation state for the central atom. With FClO_3 as a reactant, the product ClF_5 indicates that fluorinations could be achieved but not without complete oxygen loss and a concomitant reduction of the chlorine central atom. The reactions all followed the equation:



*Denotes the activated species whose excess energy is dissipated at the cold wall.

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Chloryl fluoride was also obtained from the FClO_3 reactions and in sufficient yield to suggest an initial loss of oxygen as an important step in the reaction. The yield of chloryl fluoride in the reaction of ClF_3O was low and probably arose from reactions of the substrate with the glass reactor during loading or workup.

A stepwise loss of oxygen was indicated in the fluorination of FClO_2 as some ClF_3O was obtained in one experiment. No attempt was made to determine optimum conditions for its formation. Chlorine trifluoride was not an appreciable product except at low F_2 pressures (25 mm vs the normal 50+ mm). No evidence for a higher chlorine fluoride such as ClF_7 was found.

Because of the demonstrated ability of this technique to achieve halogen fluorination, an examination of the possible oxidative fluorination of BrF_5 to BrF_7 was conducted. While it has been noted that no evidence for a species such as ClF_7 was found, the potentially lower energy necessary for bromine oxidation, coupled with the more favorable size of the Br (VII) ion, offered some promise for the experiments. Two reactions were carried out under conditions that had been found suitable for fluorination in the F-Cl-O work. Only a very slow fluorine uptake was noted at a rate much slower than with the chlorine compounds. Bromine pentafluoride was recovered unchanged along with minor quantities of BrF_4 and a trace of ClF_5 . The latter was undoubtedly due to chlorine impurities. These negative results for the possible BrF_7 are in keeping with other attempts at its preparation.

Ultraviolet Reactions

Previously it was found that ClF_3O could be formed readily from $\text{F}_2\text{-FClO}_3$, $\text{F}_2\text{-FClO}_2$, $\text{F}_2\text{-Cl}_2\text{-O}_2$, $\text{ClF}_3\text{-O}_2$, or ClF-O_2 merely by subjecting the mixtures to uv radiation at low temperature (Ref. 3). It may be recalled that rather high conversions and yields were obtained from some of the

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reactant systems. The mild conditions used ($T < -40$ C, $P < 1$ atm) suggested that similar mild conditions may be fruitful in studying other reactant systems. Accordingly, several experiments were carried out in the $\text{BrF}_5\text{-F}_2$, $\text{BrF}_5\text{-O}_2$, $\text{IOF}_5\text{-ClF}$ systems.

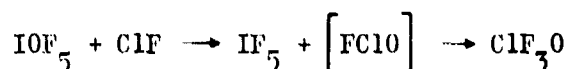
Fluorination of BrF_5 . The fluorination of BrF_5 to BrF_7 was sought through uv activation. Using the apparatus described previously (Ref. 3), four experiments were carried out. The temperatures used were from -50 to -40 C, while $\text{F}_2\text{:BrF}_5$ ratios of 1:9 were used. No evidence for a new BrF species was observed inasmuch as BrF_5 was recovered unchanged. Further, no low-temperature stable species were noted during product workup.

Reaction of IOF_5 With ClF . The facile decomposition of IOF_5 to IF_5 and O_2 is accomplished by thermal activation ($T \sim 150$ C). Despite the absence of a known decomposition mechanism for the decomposition of IOF_5 , a possibility existed that excited oxygen was an intermediate and could be capable of fixation. For this reason, IOF_5 was selected as a potential "oxygen donor" in reaction systems where new oxyhalogen fluorides were possible. If the reaction



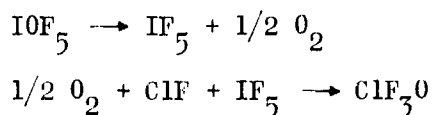
could be effected via uv activation, much less energetic radiation would be required than that required for the $\text{ClF}_3\text{-O}_2$ system.

A 1-hour irradiation of IOF_5 was sufficient for decomposing it to IF_5 and O_2 . Two experiments of IOF_5 and ClF at -60 C were then carried out and found to result in the formation of ClF_3O in a 16 percent yield. It then remained to determine whether the formation of ClF_3O was via O_2 or IOF_5 . More specifically, the choice was between:



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or

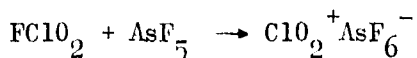
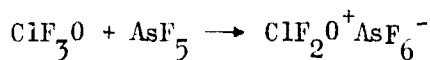


A repetition of the reaction using a stream of O_2 between the lamp and the cell resulted in a threefold decrease in the yield of ClF_3O . Thus, it appears that oxygen activation by uv is responsible for the formation of ClF_3O in the IOF_5 - ClF system.

Attempted Synthesis of Bromine Oxyfluorides. The formation of ClF_3O by the irradiation of ClF_3 and O_2 occurred readily at low temperature (-40 to -60 C). It was interesting to examine the BrF_5 - O_2 system for the synthesis of BrF_3O or BrF_5O . However, with exposure times to 3 hours, no reaction of BrF_5 was noted.

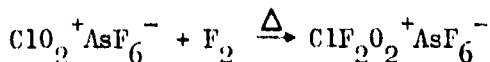
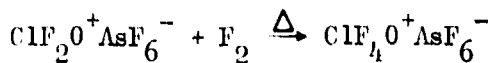
Cationic Fluorinations

The amphoteric character of ClF_3O and FClO_2 has been established since both materials form stable 1:1 complexes with arsenic pentafluoride (Ref. 3):



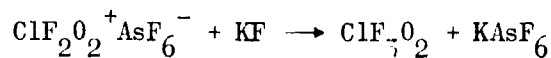
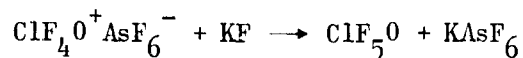
Preliminary characterization and evidence presented elsewhere in this report confirms the ionic nature of these complexes.

Fluorination reactions employing these materials were aimed at the synthesis of new cationic Cl-F-O species:



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Preparation of either of these new cations would afford intermediates from which the free, unknown chlorine oxyfluorides (ClF_5O and ClF_3O_2) might be derived:



A series of reactions were carried out using the Cl-O^- salts and elemental fluorine. All Monel equipment was employed, and the reactants were heated for 1 to 2 weeks at approximately 140 C. Each salt was subjected to F_2 pressures of 500, 900, and 2000 psi. These conditions were considered sufficient to ensure that even a slow reaction would result in a product yield large enough for easy detection.

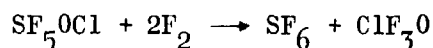
Termination of the reaction was followed by removal of gases not condensable at liquid nitrogen temperature (primarily fluorine). Vacuum fractionation of condensable materials was employed to determine if new covalent compounds were formed. The results were uniform for all experiments in that only minor quantities of CF_4 , SF_6 , and ClF_5 were observed. (These compounds are merely contaminants in the fluorine supply and not the product of the reaction.) Solids left in the cylinders were examined in the dry box and sampled for infrared analysis. In all cases, the white solid complexes were recovered unchanged. The characteristic infrared spectra for each complex were unchanged and Cl=O absorptions at frequencies higher than those in the starting compounds were not detected. Such absorptions would be expected for the more highly oxidized Cl-O cations and these bands are of sufficiently strong intensity that even low concentrations of such species would be readily detectable. Thus, fluorination of Cl=O containing cations does not occur under stringent thermal and pressure conditions.

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Fluorination of SF₅OCl

Previous work at Rocketdyne (Ref. 3) has resulted in the discovery of the new compound SF₅OCl (SF₄O + ClF $\xrightarrow{\text{CsF}}$ SF₅OCl). Since this compound belongs to the class of hypochlorites, its fluorination could yield ClF₃O according to:

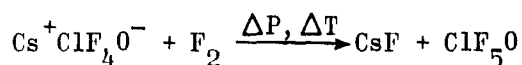


The coproduct SF₆ is compatible with ClF₃O and the reaction, if successful, could avoid some of the problems encountered in the fluorination of ClONO₂.

Two reactions between SF₅OCl and F₂ were carried out at -78 and 23 C, respectively. In both cases no fluorination of SF₅OCl was observed. However, the amount of SF₅OCl available for the experiments was insufficient to allow a liquid phase reaction. Judging from experience with the ClONO₂ - F₂ system, the presence of a liquid phase may be crucial. Hence, the fluorination of SF₅OCl should be repeated under conditions warranting the presence of a liquid phase.

Fluorination of Rb⁺ClF₄O⁻ and Cs⁺ClF₄O⁻

The fluorination of ClF₄O⁻ salts could provide the novel oxidizer, ClF₅O, according to:



This reaction would be analogous to the successful fluorination of ClF₄⁻ salts (Ref. 4) yielding ClF₅:

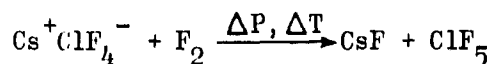


Table 1 shows the results of five runs.

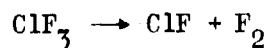
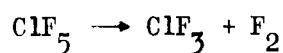
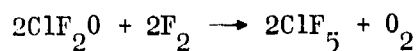
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TABLE 1

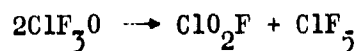
FLUORINATION OF ClF_4O^- SALTS

Starting Material, (mmoles)	Reaction Temperature, C	Volatile Reaction Products, mmoles					
		ClO_2F	ClF_3	ClF	ClF_3O	ClF_5	ΣCl
$\text{Rb}^+\text{ClF}_4\text{O}^-$ (18)	145	0.14					
	215	2.1	13.5	2.0			17.6
$\text{Cs}^+\text{ClF}_4\text{O}^-$ (20)	145	Trace			Trace		
	165	0.8			1.2		
	215	2.4	2.0		6.5	6.6	19.5

In all runs, no evidence for a new chlorine fluoride was obtained. The material balance (based on chlorine) indicated that essentially all starting material was recovered in the form of volatile products. The fact that ClF , ClF_3 , and ClF_3O could be removed as volatiles in the presence of CsF is not surprising since it is known that the reaction between these compounds in the gaseous state and solid CsF is relatively slow. However, quenching of the hot reactors, followed by immediate removal of the volatile products, is important. The formation of the observed reaction products can be rationalized in terms of the following equations:



The formation of ClO_2F could be due to the following reaction:



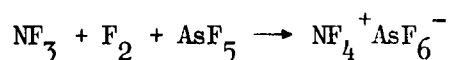
and, to a lesser degree, to the interaction between ClF_3O and incompletely passivated sections of the vacuum system.

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SYNTHESIS OF NEW OXIDIZING CATIONS

The successful synthesis of NF_4^+ containing salts from

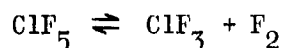


by either glow discharge (Ref. 5 through 7) or thermal activation (Ref. 8 and 9) suggests the same approach toward the synthesis of salts containing novel cations. Of the many possible cations the preparation of ClF_6^+ , BrF_6^+ , ClF_4^+ , OF_3^+ , and ArF^+ was attempted during the past period.

The ClF_6^+ Cation

Attempts were made to synthesize the BF_4^- , AsF_6^- , and SbF_6^- salts of ClF_6^+ .

In the case of BF_4^- the glow discharge technique was chosen since BF_3 and ClF_5 do not form a complex with each other. When a mixture of ClF_5 , F_2 , and BF_3 in a mole ratio of 1:1.4:1 was exposed to glow discharge at -78°C , a white solid was formed on the cold walls of the reaction vessel. Upon warming, the solid decomposed below room temperature, yielding an equimolar mixture of ClF_3 and BF_3 . Hence, the solid complex must have been $\text{ClF}_2^+ \text{BF}_4^-$ (Ref. 10 through 12). The formation of $\text{ClF}_2^+ \text{BF}_4^-$ is not surprising since in the glow discharge the following equilibrium exists:



Because ClF_3 is removed continuously from the gas phase by complex formation with BF_3 , the equilibrium is shifted toward the right side.

An attempt to achieve the synthesis of $\text{ClF}_6^+ \text{BF}_4^-$ by the high-temperature/high-pressure technique was unsuccessful. When a mixture of BF_3 , F_2 , and ClF_5 in a mole ratio of 1:2.7:2 was heated in a Monel cylinder to 95°C for 160 hours under an autogenous pressure of 450 psi, no solid formation was observed.

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Preliminary data on the synthesis of $\text{ClF}_6^+ \text{AsF}_6^-$ had been reported in our last report (Ref. 3). Four additional experiments were carried out in the mean time for the ClF_5 , F_2 , AsF_5 system. However, the preliminary data could not be reproduced. Variation of the mole ratio of the starting materials, pressure, heating time, and reaction temperature did not result in the formation of the desired salt, $\text{ClF}_6^+ \text{AsF}_6^-$. Table 2 summarizes the data obtained in these four runs in addition to those obtained in the original experiment.

Similar attempts to substantiate the existence of a $\text{ClF}_6^+ \text{SbF}_6^- \cdot x\text{SbF}_5$ salt failed. Three experiments were carried out in addition to the one described in Ref. 3. The results of these runs are summarized in Table .

The fact that in run 2 (Table 3) SbF_6^- and not $\text{Sb}_2\text{F}_{11}^-$ or higher polymeric anions had formed was not surprising since ClF_5 had been used in excess. Also, at higher temperatures, the formation of SbF_6^- is favored over that of the polymeric anions. Again the breakdown of ClF_5 was observed as discussed previously and was accompanied by shifting of the equilibrium. It appears that Lewis acids or bases may possibly catalyze the decomposition of ClF_5 into lower fluorides plus fluorine.

The products of runs 1 and 4 were very similar as far as their infrared spectra were concerned. In run 4, about 2 grams of the solid had deposited in the upper section of the reaction vessel. This material seemed to be of high purity, and its infrared spectrum indicated the absence of ClF_4^+ salt. The spectrum was nearly identical with that of the product of run 1 after subjecting it to pyrolysis in vacuo at 180 C. This compound, when mixed with a fourfold excess of finely powdered, dry CsF and heated in vacuo, yielded ClF_3 as the only volatile product. Thus, it appears that the product of run 1 (showing an infrared spectrum similar to that of run 1 in the $\text{AsF}_5 - \text{F}_2 - \text{ClF}_5$ system and similar to that of the product ascribed by the Midwest Research Institute Group to $\text{ClF}_6^+ \text{BiF}_6^-$, Ref. 13, is rather $\text{ClF}_2^+ \text{Sb}_2\text{F}_{11}^-$, and not a ClF_6^+ containing salt.

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TABLE 2
 $\text{ClF}_5 - \text{F}_2 - \text{AsF}_5$ SYSTEM

Run No.	Mole Ratio, $\text{ClF}_5:\text{F}_2:\text{AsF}_5$	Reaction			F_2 Consumption, Mole % Based on ClF_5	Solid Product, g, Infrared Spectrum, cm^{-1}
		Temperature, C	Time, days	Pressure, psi		
1	2:2:1	140	3	650	0	0.5 g IR: 821, 767, 695, 608, 516, 430, 400
2	2:2:1	160	3	650	19% of F_2 Generated by Decomposition of $\text{ClF}_5 \longrightarrow \text{ClF}_3 + \text{F}_2$	0.2 g IR: Mainly Ni^{++} , Cu^{++} AsF_6^- Salts
3	3.5:8.5:1	125	10	800	< 0.3	Trace
4	3.5:8.5:1	145	10	800	< 0.3	Trace IR: $\text{ClO}_2^+ \text{AsF}_6^-$
5	1:5:2	140	5	1000	7	Trace IR: $\text{ClO}_2^+ \text{AsF}_6^- + \text{Ni}^{++}$ and Cu^{++} Salts

TABLE 3
ClF₅ - F₂ - SbF₅ SYSTEM

Run No.	Mole Ratio, ClF ₅ :F ₂ :SbF ₅	Reaction			F ₂ Consumption, Mole % Based on ClF ₅	Solid Product
		Temperature, C	Time, days	Pressure, psi		
1	1:5:3	175	40	900	55	ClF ₂ ⁺ Sb ₂ F ₁₁ ⁻ + ClF ₄ ⁺ Sb ₂ F ₁₁ ⁻ + Ni ⁺⁺ Cu ⁺⁺ Sb ₂ F ₁₁ ⁻
2	2:5:1	225	7	900	Amount of F ₂ Equivalent to SbF ₅ was Generated	ClF ₂ ⁺ SbF ₆ ⁻
3	1:5:3	140	3	700	0	Was not Investigated
4	1:5:3	160	25	800	33	Ni ⁺⁺ , Cu ⁺⁺ Sb ₂ F ₁₁ ⁻ ClF ₂ ⁺ Sb ₂ F ₁₁ ⁻ + ClF ₄ ⁺ Sb ₂ F ₁₁ ⁻ Solid + CsF → ClF ₃

This conclusion is further supported by the Raman spectrum of the solid. It shows, in addition to the bands characteristic for the $\text{Sb}_2\text{F}_{11}^-$ anion, only bands coinciding with those of the infrared spectrum. In the case of an octahedral ClF_6^+ cation, these bands should be mutually exclusive. Furthermore, the frequency shift of only about 10 cm^{-1} appears too small for the antisymmetric stretching vibration of the hypothetical ClF_6^+ cation when compared to that of ClF_2^+ and ClF_4^+ . However, this shift of 10 cm^{-1} could well be due to the change in anion when comparing $\text{ClF}_2^+\text{SbF}_6^-$ with $\text{ClF}_2^+\text{Sb}_2\text{F}_{11}^-$.

Summarizing, it can be said that no data could be obtained supporting the existence of the postulated ClF_6^+ salts. Many of the properties of these compounds can be accounted for on the basis of the ClF_2^+ cation combined with polymeric anions.

The BrF_6^+ Cation

The preparation of $\text{BrF}_6^+\text{SbF}_6^- \cdot x\text{SbF}_6^-$ was attempted using the high-pressure/high-temperature method. A mixture of BrF_5 , F_2 , and SbF_5 in a mole ratio of 1:5:3 was heated to 140°C for 5 days under an autogenous pressure of 1000 psi. The F_2 consumption was 41 percent, based on BrF_5 . Spectroscopic investigation of the solid reaction product showed it to consist essentially of $\text{BrF}_5 \cdot 2\text{SbF}_5$ complex in addition to some Ni^{++} and Cu^{++} fluoroantimonates. A sample of $\text{BrF}_5 \cdot 2\text{SbF}_5$ was prepared from BrF_5 and SbF_5 and characterized for comparison.

The ClF_4O^+ Cation

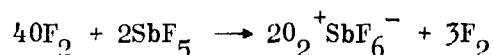
A mixture of ClF_3O , F_2 , and SbF_5 in a mole ratio of 1:10:5 was heated to 135°C for 6 days under an autogenous pressure of 600 psi. The F_2 consumption was 43 percent, based on ClF_3O . Spectroscopic investigation of the solid residue showed it to be mainly $\text{ClF}_2\text{O}^+\text{SbF}_6^-$ (after removing excess of SbF_5 at 130°C in vacuo) in addition to some $\text{Sb}_2\text{F}_{11}^-$ and Ni^{++} and Cu^{++} salts. No evidence for the formation of the desired salt, $\text{ClF}_4\text{O}^+\text{SbF}_6^-$, was obtained.

The ArF^+ Cation

Argon, F_2 , and SbF_5 in a mole ratio of 1:2:1 were combined in a Monel cylinder and heated to 135 C for 6 days under an autogenous pressure of 800 psi. Fluorine and Ar were recovered in nearly quantitative yield and no evidence for the formation of the desired $\text{ArF}^+\text{SbF}_6^-$ complex was obtained.

The OF_3^+ Cation

A mixture of OF_2 , F_2 , and SbF_5 in a mole ratio of 1:5:3 was heated to 175 C for 42 days under an autogenous pressure of 600 psi. After removal of the material volatile at ambient temperature, 8.6 g of a solid was obtained, which was characterized by elemental analysis, infrared, Raman, and ESR spectroscopy as a mixture of $\text{Ni}(\text{Sb}_2\text{F}_{11})_2$, $\text{Cu}(\text{Sb}_2\text{F}_{11})_2$ and $\text{O}_2\text{Sb}_2\text{F}_{11}$. The formation of $\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$ in this reaction is not surprising since OF_2 is known (Ref. 14) to interact with SbF_5 according to:



The Raman band observed for O_2^+ at 1865 cm^{-1} agrees well with the value of 1862 cm^{-1} recently reported for $\text{O}_2^+\text{SbF}_6^-$ (Ref. 15). It should be noted that the frequencies reported in the literature for $\text{Sb}_2\text{F}_{11}^-$ (Ref. 16 and 17) appear to be erroneous.

STRUCTURAL INVESTIGATIONS

Raman Spectrum of Liquid ClF_3O

The Raman spectrum of liquid ClF_3O was recorded and the degree of depolarization of the bands was measured. The number of observed bands and their depolarization agrees only with the trigonal bipyramide model of symmetry C_s suggested earlier (Ref. 3).

The suggested occurrence of a double and triple coincidence of bands in the infrared spectrum (Ref. 3) at 680 and 490 cm^{-1} respectively, was confirmed. Table 4 lists the observed frequencies together with their assignment.

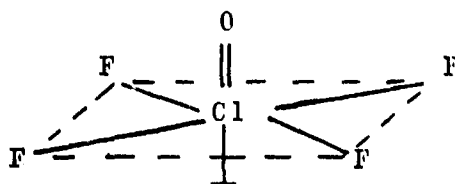
Vibrational Spectra of the ClF_2O^+ Cation

The Raman spectrum of $\text{ClF}_2\text{O}^+\text{AsF}_6^-$ and the infrared spectrum of $\text{ClF}_2\text{O}^+\text{BF}_4^-$ and $\text{ClF}_2\text{O}^+\text{SbF}_6^-$ have been recorded. The tentative assignments for ClF_2O^+ suggested in the previous report (Ref. 3) on the basis of the incomplete infrared spectrum of $\text{ClF}_2\text{O}^+\text{AsF}_6^-$ were confirmed. The two missing fundamentals, ν_4 and ν_6 , were shown to occur at 371 and 406 cm^{-1} , respectively. The observed data confirm that ClF_2O^+ has symmetry C_s ; i.e., its structure is derived from a tetrahedron with a localized free electron pair occupying one corner.

Table 5 shows the observed frequencies together with their assignments. Comparison of the data obtained for ClF_2O^+ with those reported (Ref. 18) for isoelectronic SOF_2 shows excellent agreement.

Vibrational Spectra of the ClF_4O^- Anion

The far infrared and Raman spectra of $\text{Rb}^+\text{ClF}_4\text{O}^-$ and $\text{Cs}^+\text{ClF}_4\text{O}^-$ have been recorded. Table 6 lists the observed frequencies together with their assignments for point group C_{4v} . For comparison, the vibrational spectra of isoelectronic XeOF_4 (Ref. 19), ClF_4^- (Ref. 20), and ClF_5 (Ref. 19 and 20) are included. The agreement between the spectra of these compounds is relatively good (except for the 430 cm^{-1} infrared band of ClF_4^- , which is probably incorrect). There is no doubt that ClF_4O^- has the structure suggested previously (Ref. 3) on the basis of the incomplete infrared spectrum:



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TABLE 4

VIBRATIONAL SPECTRUM OF ClF_3O

<u>IR Gas</u>	<u>RA Liquid</u>	<u>Assignment (Cs)</u>
1227.8 1224.4 - 1218.0 - 1213.4	s 1229 (1) pol.	$\nu_1 (a') \nu_{\text{Cl}=\text{O}}$
700.5 684.4 - 675.6 - 665.6	vs 702 (3) pol. too weak to be observed dp	$\nu_2 (a') \nu_{\text{Cl}-\text{F} \text{ eq.}}$ $\nu_7 (a'') \nu_{\text{as}} \text{ F-Cl-F ax.}$
501 491 482	ms 494 (0.1) pol. 478 (3) pol. 456 (6) pol.	$\nu_4 (a') \delta \text{ F-Cl=O}$ $\nu_3 (a') \nu_{\text{sym}} \text{ F-Cl-F ax}$
	462 (10) dp	$\nu_8 (a'') \delta_{\text{wag}}$
412 404	w 407 (0.2) pol.	$\nu_5 (a') \delta \text{ F-Cl-F}$
323 313	m 316 (0.2) pol.	$\nu_6 (a') \delta \text{ F-Cl-F}$
245 230	mw 232 (1) dp	$\nu_9 (a'') \tau$

<u>Observed</u>	<u>Calculated</u>	<u>Assignment</u>
899 vw =	491 + 408 = 899	$\nu_3 + \nu_5 \text{ or } \nu_4 + \nu_5$
980 W =	2 x 491 = 982	$2 \times \nu_3, 2 \times \nu_4, \nu_3 + \nu_4$
1161 mw =	491 + 676 = 1167	$\nu_3 + \nu_7, \nu_4 + \nu_7$
1372 mw =	676 + 700 = 1376	$\nu_7 + \nu_2$
1899 vw =	676 + 1221 = 1897	$\nu_7 + \nu_1$
2436 w =	2 x 1221 = 2442	$2 \times \nu_1$

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TABLE 5

VIBRATIONAL SPECTRA OF ClF_2O^+ SALTS COMPARED

Observed Frequencies, cm ⁻¹						
SO ₂ F ₂			ClF ₂ O ⁺ BF ₄ ⁻	ClF ₂ O ⁺ AsF ₆ ⁻		ClF ₃
IR (g)	RA (g)	RA (l)	IR	IR	RA	
1341 } 1331 } s	1339 } 1329 } (10)	1308 (10)	1334 s } 1322 mw } 1295 m }	1331 ms } 1319 mw }	1333 (2) } 1320 (1) }	1331 1311
			1140-980 vs, br			
			771 w	820 sh		
808 s	808 (10)	804 (6)	737 m	750 s, br	758 (3) br	745
747 vs	747 (4)	716 (6)	692 s	690 vs	696 (1)	710
				690 vs		658
					674 (10)	
				561 ms	563 (3)	559
530 w	530 (8)	528 (8)	532 w } 522 sh }	511 ms	511 (2)	509
393 w	390	399 (7)	405 mw	400 s	406 (2) br	402
				400 s		
378 vs	390	380 (5)		374 sh	371 (4)	
					371 (4)	

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TABLE 5

OF ClF_2O^+ SALTS COMPARED TO THAT OF SOF_2

		Assignment		
O^+AsF_6^-	$\text{ClF}_2\text{O}^+\text{SbF}_6^-$	OXF_2 (C_s)	YF_6^- (O_h)	BF_4^- (T_d)
RA	IR			
$\left. \begin{array}{l} 1333 \text{ (2)} \\ 1320 \text{ (1)} \end{array} \right\}$	$\left. \begin{array}{l} 1331 \text{ s} \\ 1319 \text{ mw} \end{array} \right\}$	ν_1 (A')		$\nu_1 + \nu_4$ (F_2) $\rho \nu_3$ (F_2)
			$\nu_2 + \nu_6$ ($\text{F}_{1u} + \text{F}_{2u}$)	ν_1 (A_1)
br 758 (3) br	745 s	ν_2 (A')		
696 (1)	710 s	ν_5 (A'')		
	658		ν_3 (F_{1u})	
674 (10)			ν_1 (A_{1g})	
563 (3)	559 mw		ν_2 (E_g)	ν_4 (F_2)
511 (2)	509 m	ν_3 (A')		
406 (2) br	402 mw	ν_6 (A'')		
			ν_4 (F_{1u})	
371 (4)		ν_4 (A')		
371 (4)			ν_5 (F_{2g})	

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TABLE 6

VIBRATIONAL SPECTRA OF ClF_4O^- SALTS COMPARED

ClF_5		ClF_4^-		$\text{Rb}^+\text{ClF}_4\text{O}^-$		$\text{Cs}^+\text{ClF}_4\text{O}^-$
IR	RA	IR	RA	IR	RA	IR
[712]	709 (3)	--	--	1208 m	1211 (0.7)	1197 m
732 vs	(-)	745 vs	--	590 vs, br	592 (0.1)	580 vs, br
--	[480]	--	--	550 vs, br	548 (0.5)	550 vs, br
541 m	538 (1)	--	505 (10)	462 w	461 (10.0)	463 mw
486 s	480 (10)	486 s	--	416 m 401 m	414 (2.3)	415 m
--	(346 calculated)	--	--	--	(393) (0.1)	--
--	480 (10)	--	417 (10)	349 w	347 (4.1)	347 w
--	375 (1)	--	288 (1)	285 vw	283 (1.5)	284 vw
302 s	296 (0+)	430 mw	--	(-)	207 (0.8)	(-)

TABLE 6

 ClF_4O^- SALTS COMPARED TO THOSE OF XeOF_4 , ClF_4^- , AND ClF_5

RA	$\text{Cs}^+\text{ClF}_4\text{O}^-$		XeOF_4		Assignment for XOF_4 for Point Group C_{4v}
	IR	RA	IR	RA	
(0.7)	1197 m	1201 (0.8)	926 s	920 (2)	$\nu_1 (A_1) \nu_X = 0$
(0.1)	580 vs, br	589 (0.3)	608 vs	(w)	$\nu_7 (E) \nu_{as} \text{XF}_4$
(0.5)	550 vs, br	559 (1.4)	361 s	365 (2)	$\nu_8 (E) \delta \text{FXO}$
(10.0)	463 mw	458 (10.0)	576 m	567(10)	$\nu_2 (A_1) \nu_s \text{XF}_4$
(2.3)	415 m	413 (4.4)	294 s	285 (0+)	$\nu_3 (A_1) \delta_s$ out of plane
) (0.1)	--	394 (0.2)	--	230 (calculated)	$\nu_5 (B_1) \delta_{as}$ out of plane
(4.1)	347 w	347 (8.3)	--	527 (4)	$\nu_4 (B_1) \nu_{as} \text{XF}_4$
(1.5)	284 vw	282 (0.6)	--	233 (1)	$\nu_6 (B_2) \delta_s$ in plane
(0.8)	(-)	198 (0.7)	(-)	161 (0+)	$\nu_9 (E) \delta'_{asp}$ in plane

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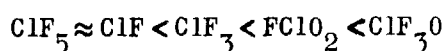
Vibrational Spectra of $\text{ClO}_2^+\text{AsF}_6^-$

The Raman spectrum of $\text{ClO}_2^+\text{AsF}_6^-$ has been recorded. It confirms the C_{2v} structure suggested previously (Ref. 3) for ClO_2^+ . The observed frequencies together with their assignment are listed in Table 7. For comparison, the spectrum of isoelectronic SO_2 (Ref. 21) is included in Table 7.

The $\text{Cl}^{35}\text{-Cl}^{37}$ isotope splitting has been determined for ClO_2^+ under high resolution conditions. It was found to be $13.96 \pm 0.20 \text{ cm}^{-1}$ for ν_3 and $5.55 \pm 0.10 \text{ cm}^{-1}$ for ν_1 . These data will allow the calculation of a General Valence Force Field for ClO_2^+ .

 $\text{ClO}_2^+\text{BF}_4^-$

The formation of the 1:1 complex of FClO_2 and BF_3 has been reported, but without quantitative data (Ref. 22). The preparation was repeated and it was verified that the material is indeed an equimolar complex. Dissociation pressure measurements at several temperatures were made to arrive at an indication of the relative Lewis base strength of this complex compared to related chlorine fluoride and chlorine oxyfluoride materials. The order established from these data and those reported for related complexes (Ref. 2 and 23) is in order of increasing stability:



Perchloryl fluoride does not form complexes with Lewis acids and no data on fluorine perchlorate have been reported.

The dissociation pressure/temperature data for $\text{ClO}_2^+\text{BF}_4^-$ are represented by the equation, $\log p_{\text{mm}} = 11.1482 - 2623.1/T$. Extrapolation gives a dissociation pressure of 760 mm at 44.1 C. A $\Delta H_D^0 = 24.01 \text{ Kcal mole}^{-1}$ was obtained from the slope of the $\log p_{\text{mm}}$ vs T^{-1} curve. From the $\Delta F_{298}^0 = -RT \ln K_p(\text{atm})$ relation, a free energy change $\Delta F_{298}^0 = 2.26 \text{ Kcal mole}^{-1}$ was calculated. An entropy change $\Delta S_{298}^0 = 72.92 \text{ cal deg}^{-1} \text{ mole}^{-1}$ was obtained

TABLE 7

VIBRATIONAL SPECTRUM OF $\text{ClO}_2^+\text{AsF}_6^-$ COMPARED TO THAT OF SO_2

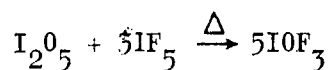
Observed Frequencies, cm^{-1}		Assignment for	
SO_2	$\text{ClO}_2^+\text{AsF}_6^-$	$\text{ClO}_2^+ (\text{C}_{2v})$	$\text{AsF}_6^- (\text{O}_h)$
IR	IR	RA	
1362	1296 ms 1282 m	1297 (1)	$\nu_3 (\text{B}_1)$
1151	1044 mw 1038 w	1046 (10) 1040 (4)	$\nu_1 (\text{A}_1)$
	819 vw	--	$\nu_2 + \nu_6 (\text{F}_{1u} + \text{F}_{2u})$
	691 vs	--	$\nu_3 (\text{F}_{1u})$
	--	684 (8)	$\nu_1 (\text{A}_{1g})$
	566 mw	570 (5)	$\nu_2 (\text{E}_g)$
518	521 m	522 (3)	$\nu_2 (\text{A}_1)$
	400 s	--	$\nu_4 (\text{F}_{1u})$
	--	372 (5)	$\nu_5 (\text{F}_{2g})$

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from $\Delta S_T^0 = (\Delta H^0 - \Delta F_T^0) T_{-1}^{-1}$. A heat of formation for the solid complex, $\text{ClO}_2^+\text{BF}_4^-$, was calculated as $\Delta H_{f298}^0 = -303 \text{ kcal mole}^{-1}$ using an estimated ΔH_{f298}^0 for $\text{FClO}_2(\text{g}) = -7 \text{ kcal mole}^{-1}$. The heat of dissociation for the $\text{FClO}_2\text{-BF}_3$ complex is comparable to that of other reported chlorine fluoride-Lewis acid complexes (Ref. 3 and 24). These data, together with the low-temperature infrared spectrum of the $\text{ClO}_2\text{F}\cdot\text{BF}_3$ adduct prove that this material also is ionic, and not a simple associated adduct as has been speculated (Ref. 25).

IODINE OXYFLUORIDES

Although several iodine oxyfluoride compositions have been reported (Ref. 26) very little information is available on the nature and chemistry of the compounds. Preliminary work to obtain this information was reported (Ref. 3) on the supposed IOF_3 . The preparative reaction is:



It has not been possible to achieve the complete conversion indicated in the equation. Weight gains corresponding to 75 to 85 percent of the theory were the maximum values obtained, and those only when purified IF_5 was used. The product obtained, although undoubtedly not pure IOF_3 , does exhibit a distinct infrared spectrum whose principal bands are consistent with the formulation $\text{IO}_2^+\text{IF}_6^-$.

The best conversions to IOF_3 were obtained on heating at 110 C for approximately 1 week, followed by cooling to room temperature for 2 days or more prior to removal of the excess IF_5 . Attempts to speed this process were made by eliminating the IF_5 purification, raising the reaction temperature to 135 C, and shortening the time. Reactions carried out in this manner failed to yield any appreciable amounts of IOF_3 but gave slightly impure FIO_2 . Purification of the FIO_2 was effected by pyrolysis at 110 C. Pyrolysis of IOF_3 at 110 C in vacuo also resulted in the formation of FIO_2 by liberation of IF_5 . The infrared spectra (Table 8) and fluorine analyses of the FIO_2 prepared in these two ways were the same. The analyses for the two samples gave F = 10.77 and 11.02, respectively, compared to the theoretical F = 10.67 for FIO_2 . The only difference in the samples was one of color, the IOF_3 pyrolysis product being white, while the sample synthesized directly has a light tan color. The direct preparation of FIO_2 has been successfully run on a 7-g scale.

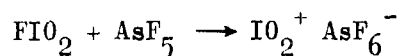
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TABLE 8

INFRARED BANDS OF FIO_2

cm^{-1}	Relative Intensity
863	sh
840	s
795	s
725	s
565	s
540	w

Attempts have been made to prepare derivatives of FIO_2 as a means of chemical characterization. In addition, the derivatives could provide information on the spectral characteristics of the various iodine oxide and oxyfluoride ions and, thereby, aid in the overall identification of species in this series of materials. For example, with arsenic pentafluoride, a probable reaction is:



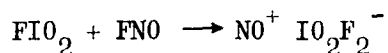
This iodyl cation complex would serve to identify the infrared bands attributable to the IO_2^+ ion because those of the AsF_6^- ion are well known.

Efforts to prepare this complex have been made with and without a solvent. With the solvents CH_3CN and CCl_4 , it was observed that a slow reaction occurred at ambient temperature, causing discoloration of the solvent but with little AsF_5 uptake. Analysis of the gaseous products indicated that either or both the FIO_2 and AsF_5 had reacted with the solvent. With CH_3CN , only a pasty brown solid was recovered. Similar results were found when BF_3 was used in place of AsF_5 . Experiments with other solvents such as HF and CFCl_3 are planned.

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Although it has been stated that FIO_2 does not react with AsF_5 (Ref. 27) without solvent, this is not totally correct. A sample of FIO_2 with a twofold excess of AsF_5 has been found to be slowly reacting. After 5 weeks, 62 percent of the AsF_5 theoretically needed for a 1:1 complex has been absorbed. This reaction is continuing to obtain a more quantitative conversion. A reasonably pure product from the reaction will be of assistance in confirming the nature of the solvent-produced complexes.

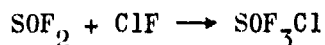
The reaction of FIO_2 with FNO was examined to determine if the IO_2F_2^- ion could be readily attained:



Such a species could function as a suitable precursor to the unknown compound, IF_3O_2 . Mixing of the materials between -80 and 0°C resulted in a gradual formation of NO_2 . The formation of NO_2 indicated that fluorination of the FIO_2 occurred, but was accompanied by oxygen abstraction from the FIO_2 . No volatile I-F or I-O-F compounds were noted. Thus, any fluorination of FIO_2 or an ionic species such as IO_2F_2^- must be done with mild fluorinating agents that do not have an affinity for oxygen. Possible agents are KrF_2 and CF_3OF .

REACTIONS OF ClF

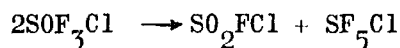
Chlorine monofluoride has been shown (Ref. 3) to be capable of oxidation and substitution reactions in which chlorine is retained in the product. Continuing interest in the chemistry of this and other halogen fluorides prompted an examination of the reaction of ClF and SOF_2 as a possible route to the unknown, unsymmetrical compound SOF_3Cl :



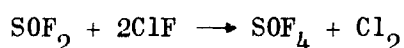
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Such a compound might be expected to be unstable and disproportionate as follows:



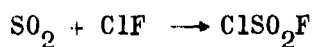
This reaction was examined at -80 C and at room temperature with SOF_2 and ClF in 1:1 and later 1:2 stoichiometries. It was found, uniformly, that SOF_4 was the only new S-O-F compound produced. Thus, with 1:1 reactant conditions, one-half the SOF_2 was converted to SOF_4 and the remainder recovered unchanged. With 1:2 reactant mixtures a nearly quantitative conversion to SOF_4 was achieved:



No indication for an unsymmetrical product or disproportionation products was found.

The ability of ClF to effect the above-noted oxidation readily, even at -80 C, exemplifies its strong oxidizing power. Previous fluorinations of SOF_2 to SOF_4 have been reported only with elemental fluorine alone (Ref. 28) or in the presence of AgF_2 (Ref. 29). Thus, this reaction is the first reported in which a practical synthesis of SOF_4 is achieved without the use of elementary fluorine.

The interaction of SO_2 and ClF also was examined as a method of preparing ClSO_2F . The desired reaction was realized; a near-quantitative conversion was obtained on warming a mixture of SO_2 and excess ClF from -196 C to ambient temperature:



Only a negligible quantity of SO_2F_2 was found and, thus, ClF must react much faster with SO_2 than with the product ClSO_2F . The simplicity and excellent results of this procedure make it an attractive alternative to previously reported synthesis of ClSO_2F (Ref. 26).

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EXPERIMENTAL DETAILS

GENERAL CONSIDERATIONS

The experimental work, unless otherwise mentioned, was carried out in metal/Teflon vacuum systems and in the inert atmosphere of glove boxes. The fluorine and chlorine pentafluorine were produced in Rocketdyne's pilot plant. The arsenic and antimony pentafluoride were obtained from Ozark-Mahoning and were purified by distillation or vacuum condensation before use.

GLOW DISCHARGE FLUORINATION

A Pyrex discharge tube with copper electrodes and Fisher-Porter valves was built into a closed-loop system containing an all-glass/Teflon recirculating pump (Ref. 30) and a Heise gage for pressure measurement. Fluorine was metered into the loop, as required, to maintain the desired pressure. The discharge tube and connecting lines were passivated and dried by treatment (three times) with ClF_3 prior to each experiment. The substrate to be used was freshly fractionated before a measured amount was frozen at -196°C into the bottom of the tube, which placed it on the walls in the discharge zone. A 15,000-volt neon transformer was used as a voltage source. Preliminary experiments (Table 9) indicated that the best fluorination results were obtained at unreduced house-line inputs. No contact of the materials with unpassivated metal or surfaces exposed to the atmosphere occurred at any point in the experiment.

CATIONIC FLUORINATIONS

Arsenic pentafluoride complexes of ClF_3O and FClO_2 were prepared and determined to be 1:1 salts. Weighed samples of the salts were placed in 95-ml, Monel cylinders that had been prepassivated. Fluorine was measured and loaded into the cylinders by condensation at -196°C . The closed cylinders were then heated in an oven at 140°C for 1 to 2 weeks. After removal of -196°C noncondensables, the condensable products were vacuum fractionated and analyzed. The solids were visually examined and infrared samples prepared in the glove box.

TABLE 9

GLOW DISCHARGE FLUORINATIONS

Run No. 1	Substrate Used	Amount Used, cc	Time, hours	F ₂ Pressure, mm	Input Voltage	Substrate Recovered, percent	Other Cl Products, percent			
							ClF ₃	ClF ₅	ClF ₃ O	FClO ₂
1	ClF ₃ O	106	3	80	120	77.5		18.5		4
2**	ClF ₃ O	101	3.5	70	120			11		13
3	ClF ₃ O	84.5	3.5	50	120	86.5	1	9		4
4	FClO ₂	55.5	1.8	60	120	67.5		30	1.5	
5	FClO ₂	72.9	3.3	25	120	83.5	5	11.5		
6	FClO ₃	75.6	2.0	60	120	74		15		11
7	FClO ₃	79.4	3.0	70	120	50		37		13

NOTE: SiF₄ and O₂F₂ was formed in all reactions, with some CF₄ and SF₆

*Average pressure ± 5 mm

**System leak during workup

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FLUORINATION OF SF_5OCl

The SF_5OCl was purified by fractional condensation prior to use and 1.79 mmoles were combined at -196°C with 13.4 mmoles of fluorine in a passivated 30-ml stainless-steel cylinder. The cylinder was kept for 47 days at -78°C . The volatiles at -196°C were removed and the contents of the cylinder subjected to fractional condensation through a series of -78° , -95° , -142° , and -196°C traps. Except for a trace of SF_4O , only unreacted starting materials were recovered.

In a second experiment, the contents of the cylinder were kept for 10 days at room temperature. Again, only unreacted SF_5OCl and a trace of SF_4O were recovered.

FLUORINATION OF ClF_4O^- SALTS

All fluorinations were carried out in passivated 30-ml stainless-steel cylinders at a fluorine pressure between 600 and 800 psi. The heating periods were always from 1 to 5 days. The reaction products were worked up by fractional condensation in the vacuum line, measured volumetrically, and identified by infrared spectroscopy.

SYNTHESIS OF NEW OXIDIZING CATIONS

The experimental technique used for all these reactions were basically the same. Hence, only a general description of the technique will be given. Compounds were identified by vibrational spectroscopy and elemental analysis. The materials balances were always checked by measuring volatile products volumetrically and by weighing the nonvolatiles. Generally, the material balances were quite good.

Infrared spectra were recorded on a Perkin Elmer 337 and a Beckman IR-7 spectrophotometer with NaCl and CsI interchange. For gases, a 5-cm Monel cell equipped with AgCl windows was used. In the case of solids, the dry-powder technique between thin AgCl plates was applied. Raman spectra were recorded using a Spectra-Physics model 125 laser as a source of ~ 80 mw of exciting light at $6328 \overset{0}{\text{\AA}}$ and a Baird-type 1310 interference filter. The scattered light was analyzed with a Spex model 1400 double monochromator, a photomultiplier cooled to -25 C, and a d-c ammeter. Pyrex glass tubes (7-mm OD), with a hollow inside glass cone for variable sample thicknesses, were used as sample containers. All reactions were carried out in Monel reactors equipped with pressure gages. The cylinders were heated by placing them in an electrically heated furnace.

STRUCTURAL INVESTIGATIONS

The instruments and sampling techniques used were described in the previous paragraph. The stainless-steel cell used for recording the Raman spectrum of liquid ClF_3O had Teflon O-rings and sapphire windows. Its design is similar to that of a cell described in the literature (Ref. 31). Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics.

PREPARATION OF $\text{ClF}_2\text{O}^+ \text{BF}_4^-$

Measured quantities of ClF_3O (72.1 cc, 3.22 mmole) and BF_3 (80.2 cc, 3.58 mmole) were separately condensed into a Teflon/stainless-steel traps attached to a Heise gage. On warming to ambient temperature, a white solid formed that was pumped on at ambient temperature for a short time. The volatile material recovered during this pumping was pure BF_3 (7.1 cc, 0.32 mmole), as indicated by its infrared spectrum. Thus, the reaction gave a 1:1 complex as indicated by the observed $\text{ClF}_3\text{O}:\text{BF}_3$ combining ratio of 1:1.04. After standing at ambient temperature for some time, no pressure over the solid was detected.

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PREPARATION OF $\text{ClO}_2^+ \text{BF}_4^-$

Measured quantities of FClO_2 (42.2 cc, 1.88 mmole) and BF_3 (64.0 cc, 2.86 mmole) were condensed into a prepassivated, Teflon, stainless-steel traps attached to a Heise gage. The total volume was approximately 75 cc. On warming to -78°C and higher, a white solid was formed. After recooling to -78°C , the solid was pumped on until no additional material was removed. In this way, 21.0 cc (0.94 mmole) of BF_3 was obtained. Thus, the solid was found to be an equimolar complex of FClO_2 and BF_3 , as the observed combining ratio was 1:1.02. The complex dissociated on warming. Dissociation pressures were measured with the Heise gage at several temperatures obtained by slush bath cooling and measured by thermocouple. The observed dissociation pressure/temperature values were (given as $^\circ\text{K}$, mm Hg): 249.9, 4.5; 261.6, 13; 273.2, 35; 280.4, 62; 286.4, 98; 288.2, 112; and 295.3, 182. A second, larger preparation on which dissociation pressure/temperature readings were made confirmed these values within experimental error.

REACTIONS OF ClF

Thionyl fluoride was prepared from thionyl chloride and sodium fluoride in acetonitrile (Ref. 32). A 10-ml prepassivated cylinder was loaded with 48.5 cc (2.16 mmole) of SOF_2 and an equal amount of freshly fractionated ClF at -196°C . The closed cylinder was allowed to warm to room temperature overnight before vacuum fractionation of the products was begun. Based on SOF_2 for 2ClF , 72 percent of the SOF_2 reacted and was 91 percent converted to SOF_4 . In a reaction employing the 1:2 stoichiometry and the above general conditions, SOF_2 (4.55 mmole) was converted to SOF_4 (4.38 mmole), i.e., 96 percent. An additional experiment in which a 1:1 stoichiometry was again used, but with the temperature kept at -80°C (4 weeks), a near-quantitative conversion of one-half of the SOF_2 to SOF_4 was obtained.

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Chlorine monofluoride (162 cc, 7.2 mmole) and SO_2 (127 cc, 5.67 mmole) were condensed into a 30-ml prepassivated cylinder at -196°C . The reactor was then allowed to warm to room temperature over a 3-hour period. Two vacuum fractionations yielded pure ClSO_2F (126 cc, 5.62 mmole), i.e., 99 percent. Only a trace of SO_2F_2 was found, and no unreacted SO_2 .

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REFERENCES

1. R-6258, Inorganic Halogen Oxidizers, Annual Summary Report, Contract Nonr 4428(00), Rocketdyne, a Division of North American Rockwell Corporation, Canoga Park, California, 30 July 1965, CONFIDENTIAL.
2. R-6641, Inorganic Halogen Oxidizers, Annual Summary Report, Contract Nonr 4428(00), Rocketdyne, a Division of North American Rockwell Corporation, Canoga Park, California, 31 July 1966, CONFIDENTIAL.
3. R-7547, Inorganic Halogen Oxidizers, Annual Report, Contract Nonr 4428(00), Rocketdyne, a Division of North American Rockwell Corporation, Canoga Park, California, 31 July 1968, CONFIDENTIAL.
4. D. Pilipovich, W. Maya, E. A. Lawton, H. F. Bauer, D. F. Sheehan, N. N. Ogimachi, R. D. Wilson, F. C. Gunderloy, and V. E. Bedwell, Inorg. Chem., 6, 1918 (1967).
5. K. O. Christe, J. P. Guertin, and A. E. Pavlath, Inorg. Nucl. Chem. Letters, 2, 83 (1966).
6. J. P. Guertin, K. O. Christe, and A. E. Pavlath, Inorg. Chem., 5, 1921 (1966).
7. K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, Inorg. Chem., 6, 533 (1967).
8. W. E. Tolberg, T. R. Rewick, R. S. Stringham, and M. E. Hill, Inorg. Nucl. Chem. Letters, 2, 79 (1966).
9. W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, Inorg. Chem., 6, 1156 (1967).
10. H. Selig and J. Shamir, Inorg. Chem., 3, 294 (1964).
11. K. O. Christe and A. E. Pavlath, Z. Anorg. Allgem. Chem., 335, 210 (1965).
12. K. O. Christe and W. Sawodny, Inorg. Chem., 6, 313 (1967).
13. Research on Advanced Oxidizers, Quarterly Progress Report No. 2, Contract F-4611-68-C-0010, Midwest Research Institute, Kansas City, Missouri, January 1968, CONFIDENTIAL.

14. J. B. Beal, C. Purp, and W. E. White, The Reaction of Oxygen Difluoride With Some Lewis Acids: The Preparation of Dioxygenyl Salts, presented at the Fourth International Fluorine Symposium, Estes Park, Colorado, July 1967.
15. J. Shamir, J. Binenboym, and H. H. Classen, J. Am. Chem. Soc., 90, 6223 (1968).
16. J. Weidlen and K. Dehnicke, Z. Anorg. Allgem. Chem., 348, 278 (1966).
17. J. K. Ruff, Inorg. Chem., 5, 1791 (1966).
18. E. L. Pace, and H. W. Samuelson, J. Chem. Phys., 44, 3682 (1966).
19. G. M. Begun, W. H. Fletcher, and D. F. Smith, J. Chem. Phys., 42, 2236 (1965).
20. K. O. Christe and W. Sawodny, Z. Anorg. Allgem. Chem., 357, 125 (1968).
21. R. D. Shelton, A. H. Neilson, and W. H. Fletcher, J. Chem. Phys., 21, 2178 (1953).
22. M. Schmeisser, and F. L. Ebenhöch, Angew. Chem., 66, 230 (1954).
23. H. Selig and J. Shamir, Inorg. Chem., 3, 294 (1964).
24. K. O. Christe and J. P. Guertin, Inorg. Chem., 4, 905 (1965).
25. M. Schmeisser and K. Brändle, Advances in Inorganic Chemistry and Radiochemistry, Vol. 5, Academic Press, New York, New York (1963), p. 58.
26. R. D. W. Hemmit and D. W. A. Sharp, Advances in Fluorine Chemistry, Vol. 4, Academic Press, New York, New York (1965), p. 142.
27. E. E. Aynsley and S. Sampath, J. Chem. Soc., 3099 (1959).
28. J. K. Ruff and M. Lustig, Inorg. Chem., 3, 1442 (1964).
29. F. B. Dudley, G. H. Cady, and D. F. Eggers, J. Am. Chem. Soc., 78, 1553 (1956).
30. J. Shapiro and H. Landesman, Rev. of Sci. Instr., 26, 252 (1955).
31. E. L. Gasner and H. H. Classen, Inorg. Chem., 6, 1937 (1967).
32. F. A. Fawcett, C. W. Tullock, and D. D. Coffman, J. Am. Chem. Soc., 84, 4275 (1962).

APPENDIX

Contribution from Rocketdyne, a Division of North American
Rockwell Corporation, Canoga Park, California 91304

The Difluoronitronium Cation, NF_2O^+

By Karl O. Christe and Walter Maya

Received 1968

ABSTRACT

Nitrogen oxide trifluoride forms white crystalline 1:1 adducts with the Lewis acids, BF_3 , AsF_5 , and SbF_5 . In addition to the 1:1 complex, BF_3 can form at -126° a 2:1 adduct with NF_3O . The thermal stability of these complexes decreases in the order: $\text{NF}_3\text{O}\cdot\text{SbF}_5 > \text{NF}_3\text{O}\cdot\text{AsF}_5 > \text{NF}_3\text{O}\cdot\text{BF}_3 > \text{NF}_3\text{O}\cdot 2\text{BF}_3$. The dissociation pressure - temperature relation has been measured and thermodynamic data are calculated for the process: $\text{NF}_3\text{O}\cdot\text{BF}_3(\text{s}) = \text{NF}_3\text{O}(\text{g}) + \text{BF}_3(\text{g})$. Hydrolysis of $\text{NF}_3\text{O}\cdot\text{AsF}_5$ results in the formation of $\text{NO}_2^+\text{AsF}_6^-$. Infrared and Raman measurements show that $\text{NF}_3\text{O}\cdot\text{SbF}_5$, $\text{NF}_3\text{O}\cdot\text{AsF}_5$, $\text{NF}_3\text{O}\cdot\text{BF}_3$, and $\text{NF}_3\text{O}\cdot 2\text{BF}_3$ have the ionic structures, $\text{NF}_2\text{O}^+\text{SbF}_6^-$, $\text{NF}_2\text{O}^+\text{AsF}_6^-$, $\text{NF}_2\text{O}^+\text{BF}_4^-$, and $\text{NF}_2\text{O}^+\text{B}_2\text{F}_7^-$, respectively. The NF_2O^+ cation (point group C_{2v}) has a structure similar to that of isoelectronic CF_2O . All fundamentals have been observed for NF_2O^+ .

INTRODUCTION

Several independent disclosures have been made on the synthesis, properties, and chemistry of NF_3O ¹⁻⁵. In addition, one paper⁶ dealing with the infrared spectrum and thermodynamic properties of NF_3O has been published.

The capability of NF_3O to form adducts with strong Lewis acids has been recognized by all three groups^{1,2,6} investigating this compound. Thus, Fox and coworkers⁴ reported the existence of 1:1 adducts between NF_3O and AsF_5 or SbF_5 . They suggested the ionic structures, $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ and $\text{NF}_2\text{O}^+ \text{SbF}_6^-$, respectively, for these adducts based on F^{19} nmr and incomplete infrared data. Similarly, Bartlett and coworkers⁵ reported the existence of the complex $\text{NF}_3\text{O} \cdot \text{AsF}_5$. They also proposed the ionic structure, $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ based on incomplete infrared data. Some of the chemistry of the $\text{NF}_3\text{O} \cdot \text{BF}_3$ adduct has been developed in showing that this adduct can add at low temperature the elements of fluorine to olefinic double bonds^{2,7}. In this paper we wish to report some of the data obtained for these NF_3O adducts by the Rocketdyne group. These data include the characterization of the adducts and the complete infrared spectrum of the NF_2O^+ cation.

- (1) W. Maya (Rocketdyne), U. S. Patent 3,320,147 (1967).
- (2) D. Filipovich (Rocketdyne), U. S. Patent 3,346,652 (1967).
- (3) W.B. Fox and J.S. MacKenzie, U. S. Patent 3,323,866 (1967).
- (4) W.B. Fox, J.S. MacKenzie, N. Vanderkooi, B. Sukornick, C.A. Wamser, J.R. Holmes, R.E. Sibeck, and D.B. Stewart, J. Am. Chem. Soc., **88**, 2604 (1966).
- (5) N. Bartlett, J. Passmore, and S.J. Wells, Chem. Comm., 213 (1966).
- (6) E.C. Curtis, D. Filipovich, and W.H. Moberly, J. Chem. Phys., **46**, 2904 (1967).
- (7) The chemistry of NF_3O adducts is rather interesting. Reactions in addition to the cited fluorination are known and are the subject of a forthcoming paper by D. Filipovich, R.D. Wilson, and W. Maya.

EXPERIMENTAL

Materials and Apparatus

The materials used in this work were manipulated in a well seasoned 304 stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves (Hoke Inc., 4251 F4Y). Arsenic pentafluoride (from Ozark Mahoning Co.), BF_3 (from The Matheson Co., Inc.), and NF_3O (prepared at Rocketdyne by glowdischarge¹ of a mixture of N_2 , O_2 , and F_2) were purified by fractional condensation. Antimony pentafluoride (from Ozark-Mahoning Co.) was purified by vacuum distillation at ambient temperature. Hydrogen fluoride (from The Matheson Co., Inc.) was purified by removing all volatiles at -196° , exposing the residue at ambient for 12 hours to a fluorine pressure of two atmospheres, followed by removal of all volatiles at -196° in vacuo. The purity of the starting materials was determined by measurements of their vapor pressures and infrared spectra. Owing to their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

Preparation of $\text{NF}_2\text{O}^+\text{AsF}_6^-$

In a typical experiment NF_3O (64.2 mmoles) and AsF_5 (42.7 mmoles) were combined at -196° in a U-trap. The mixture was allowed to warm up slowly until melting and reaction occurred. When the pressure inside the trap reached 760 mm the mixture was cooled again to -196° . This procedure was repeated several times until the reaction was complete. Unreacted NF_3O (21.4 mmoles) was removed by distillation at 0° . Therefore, AsF_5 (42.7 mmoles) had reacted with NF_3O (42.8 mmoles) in a mole ratio of 1:1.002, producing the complex $\text{NF}_2\text{O}^+\text{AsF}_6^-$.

Preparation of $\text{NF}_2\text{O}^+ \text{SbF}_6^-$

Antimony pentafluoride (93.6 mmoles) was transferred in the glove box to a Kel-F trap containing a Teflon coated, magnetic stirring bar. The trap was connected to the vacuum line and 30 ml of liquid HF was condensed into the trap at -196° . The contents of the trap were warmed to ambient and stirred until all the SbF_5 had dissolved in the HF. This trap was connected to a second trap by means of flexible Teflon tubing. The second trap contained liquid NF_3O (171 mmoles) at -95° . The trap containing the SbF_5 -HF solution was inverted and the SbF_5 -HF solution was slowly added to the liquid NF_3O at -95° with shaking. The mixture was kept for 16 hours at -78° . Subsequently, the HF solvent and excess NF_3O were removed by vacuum distillation at 25° . Weighing of the trap, empty and after complex formation, indicated a NF_3O to SbF_5 combining ratio of 1:1.09.

Preparation of $\text{NF}_2\text{O}^+ \text{BF}_4^-$ and $\text{NF}_2\text{O}^+ \text{B}_2\text{F}_7^-$

In a typical experiment, NF_3O (51.4 mmoles) and BF_3 (12.8 mmoles) were combined at -196° in a U-trap. The mixture was allowed to warm up slowly until melting and reaction occurred. When the pressure inside the trap reached 1000 mm the mixture was cooled again to -196° . This procedure was repeated several times until the reaction was complete. Unreacted NF_3O (45.0 mmoles) was recovered by distillation at -126° and identified by its infrared spectrum. Therefore, BF_3 (12.8 mmoles) had reacted with NF_3O (6.4 mmoles) in a mole ratio of 2:1.00, producing the complex $\text{NF}_2\text{O}^+ \text{B}_2\text{F}_7^-$.

Warming of the solid to -94.5° resulted in a pressure of about 180 mm. Removal of the volatiles at -94.5° yielded 6.4 mmoles of BF_3 , contaminated by a very small amount of NF_3O . Hence, NF_3O and BF_3 had combined in a 1:1 mole ratio, producing the complex $\text{NF}_2\text{O}^+ \text{BF}_4^-$.

Similarly, synthesis of the complex, $\text{NF}_2\text{O}^+\text{BF}_4^-$, was achieved when an excess of BF_3 (51.4 mmoles) was combined with NF_3O (6.4 mmoles) at -196° . Removal of unreacted BF_3 was very slow at -126° . Complete removal of the excess BF_3 could be achieved at -112° , however, at this temperature a small amount of NF_3O was also transferred. The amount of volatiles (38.7 mmoles) was measured by keeping the trap (in which the volatiles had been collected) at -78° during expansion of the gas into a measured volume and by correcting the observed pressure for the known dissociation pressure of $\text{NF}_2\text{O}^+\text{BF}_4^-$ at -78° (see Result section). Infrared measurements on the gas showed that it contained less than 0.1% of NF_3O . Hence, NF_3O (6.4 mmoles) had combined with BF_3 (12.7 mmoles) in a mole ratio of 1:1.98, producing the complex $\text{NF}_2\text{O}^+\text{BF}_4^-$.

Infrared measurements showed that the gas phase in equilibrium with solid $\text{NF}_2\text{O}^+\text{BF}_4^-$ at temperatures -78.6° to -54.1° consisted of NF_3O and BF_3 in a 1:1 mole ratio. (Intensity of NF_3O and BF_3 peaks always corresponded to those of an equimolar mixture).

Dissociation Pressure Measurements

The $\text{NF}_2\text{O}^+\text{BF}_4^-$ complex was prepared in a Teflon FEP U-trap being directly connected to a Heise, Bourdon tube-type gauge, (0-1500 mm \pm 0.1%). Pressures were read with a cathetometer (to an accuracy of \pm 0.2 mm) and the temperature of the cooling bath was determined with a copper-constantan thermocouple. To be certain that an equilibrium existed at each temperature reading, a sample of the gas above the solid complex was pumped off and a constant pressure was reestablished. True equilibrium existed at a given temperature if the pressures, before and after the pumping off procedure, were identical. Equilibrium pressures were always approached from below a given temperature. The best fit of $\log P$ vs. T^{-1} (in $^\circ\text{K}$) was obtained by the method of least squares.

Infrared Spectra

The infrared spectra were recorded on a Beckman Model IR-7 with CsI interchange and a Perkin Elmer Model 337 spectrophotometer in the range 700-200 and 4000-400 cm^{-1} , respectively. The spectra of gases were obtained using 304 stainless steel cells of 5 cm path length fitted with AgCl windows. The low-temperature spectra of $\text{NF}_3\text{O} \cdot x\text{AsF}_5$ and $\text{NF}_3\text{O} \cdot x\text{BF}_3$ were taken by preparing the complexes on the internal window (cooled with liquid nitrogen) of an infrared cell. The body of this cell was made from Pyrex glass, all windows being AgCl. Screw-cap metal cells with AgCl windows and Teflon FEP gaskets were used for obtaining the spectrum of $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ and $\text{NF}_2\text{O}^+ \text{SbF}_6^-$ as a dry powder at ambient temperature.

Raman Spectra. The Raman spectrum of solid $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ was recorded using a Spectra-Physics Model 125 laser as a source of ~ 80 mw of exciting light at 6328 \AA and a Baird Type 1310 interference filter (45 \AA halfwidth). The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to $\sim -25^\circ$ and a d.c. ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses were used as sample containers.

Hydrolysis of $\text{NF}_2\text{O}^+ \text{AsF}_6^-$

A thin film of solid $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ condensed on the internal, cold window of the low-temperature infrared cell was exposed briefly to atmospheric moisture. The sample was allowed to warm up to ambient and after 4 hours all volatiles were removed by pumping. The infrared spectrum of the white, solid residue left on the internal window was identical with that of a sample of $\text{NO}_2^+ \text{AsF}_6^-$.

X-Ray Powder Data

Debye-Scherrer powder patterns were taken using a Phillips Norelco instrument, Type No. 12046, with copper K α radiation and a nickel filter. Samples were sealed in Lindeman glass tubes (~ 0.3 and ~ 0.5 mm o.d.).

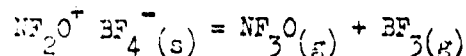
RESULTS

Synthesis

Nitrogen oxide trifluoride and AsF_5 , when mixed, produced the 1:1 complex, $\text{NF}_2\text{O}^+ \text{AsF}_6^-$, a white crystalline solid. Quantitative synthesis clearly indicates a 1:1 combining ratio. Similarly, the addition of SbF_5 (dissolved in HF) to an excess of liquid NF_3O at -95° resulted in the 1:1 complex, $\text{NF}_2\text{O}^+ \text{SbF}_6^-$. The combination of NF_3O with BF_3 at -126° produced the 1:2 complex, $\text{NF}_2\text{O}^+ \text{B}_2\text{F}_7^-$. Quantitative synthesis clearly indicates a 1:2 combining ratio. This ratio was found independent of using either NF_3O or BF_3 in excess. The 1:2 complex, $\text{NF}_2\text{O}^+ \text{B}_2\text{F}_7^-$, loses one mole of BF_3 at -95° to produce the 1:1 complex, $\text{NF}_2\text{O}^+ \text{BF}_4^-$. Quantitative synthesis and infrared measurements on the gas phase above the solid complex support the 1:1 combining ratio.

Thermochemical Properties

The complex, $\text{NF}_2\text{O}^+ \text{SbF}_6^-$, has no detectable dissociation pressure at 25° . The corresponding arsenic compound, $\text{NF}_2\text{O}^+ \text{AsF}_6^-$, has no detectable dissociation pressure at 0° , but exhibits a dissociation pressure of 4 mm at 22.1° . The 1:2 adduct, $\text{NF}_3\text{O} \cdot 2\text{BF}_3$, has no detectable dissociation pressure at -126° , but shows a dissociation pressure of about 180 mm at -94.5° . For the 1:1 adduct, $\text{NF}_2\text{O}^+ \text{BF}_4^-$, the following dissociation pressure data were observed, temperature [$^\circ\text{C}$], pressure [mm]: $-93.90, 1.8$; $-78.63, 12.5$; $-73.13, 24.0$; $-64.28, 63.0$; $-57.39, 123.5$; $-54.06, 166.0$. A plot of $\log P_{\text{mm}}$ vs. T^{-1} (in $^\circ\text{K}$) for the heterogeneous equilibrium



is a straight line. The equation

$$\log P_{\text{mm}} = 11.1025 - \frac{1914.88}{T}$$

represents these dissociation data in the temperature range -93.9 to -54.1° . By extrapolation, a dissociation pressure of one atmosphere was obtained at -36.61° . At 25° the dissociation pressure amounts to 37680 mm. From the slope of the $\log P_{\text{mm}}$ vs. T^{-1} curve $\Delta H_d^{\circ} = 17.80 \text{ kcal mole}^{-1}$ was found. From $\Delta F_d^{\circ} = -RT \ln K_p$ (atm), a free energy of change, $\Delta F_{298}^{\circ} = -3.804 \text{ kcal mole}^{-1}$, and from $\Delta S_d^{\circ} = (\Delta H_d^{\circ} - \Delta F_d^{\circ}) T^{-1}$, an entropy change, $\Delta S_{298}^{\circ} = 72.45 \text{ cal deg}^{-1} \text{ mole}^{-1}$, were found for the dissociation process at 25° . A heat of formation of $\text{NF}_2\text{O}^+ \text{BF}_4^-$ (s), $\Delta H_f^{\circ} = 323 \text{ kcal mole}^{-1}$ was calculated based upon $\Delta H_f^{\circ} = 298$ $[\text{NF}_3\text{O}(\text{g})]^9 = -33 \text{ kcal mole}^{-1}$ and $\Delta H_f^{\circ} = 298$ $[\text{BF}_3(\text{g})]^{10} = -271.6 \text{ kcal mole}^{-1}$.

Hydrolysis of $\text{NF}_2\text{O}^+ \text{AsF}_6^-$

Careful hydrolysis of $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ resulted in the formation of a white solid residue. The infrared spectrum of the solid showed four absorptions at 2360 (ms), 697 (vs), 598 (ms), and 400 (m) cm^{-1} , respectively. When solid $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ is added to excess water the hydrolysis proceeds violently.

X-Ray Powder Data

Debye-Scherrer powder patterns were obtained for $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ and $\text{NF}_2\text{O}^+ \text{SbF}_6^-$. The patterns of both compounds were too complex to allow determination of the crystal system and lattice parameters. The pattern obtained for $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ possibly contained some of the stronger lines characteristic for $\text{NO}_2^+ \text{AsF}_6^-$ ¹¹.

- (8) It is not strictly correct to infer that the measured heat of reaction for the dissociation process equals the thermodynamic heat of dissociation. This would only be appropriate if the complex were in the gas phase or if the heat of sublimation of the complex were zero. However, for convenience, ΔH_d° will be used throughout the text to mean the heat of reaction of a complete dissociation process of the type: complex(s) = gas + gas.
- (9) J.C. Weber, of our laboratories estimated this value by comparison with bond energies of known N-F and N-O-F containing compounds.
- (10) G.K. Johnson, H.M. Feder, and W.N. Hubbard, J. Phys. Chem., 70, 1 (1966).
- (11) D. Loe and A. Young, J. Am. Chem. Soc., 87, 1889 (1965).

Vibrational Spectra

Figures 1 and 2 show the infrared spectrum of the solids, $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ and $\text{NF}_2\text{O}^+ \text{SbF}_6^-$, respectively. These spectra were recorded using the dry powder technique. The observed frequencies are listed in Table I and are compared with those reported for isoelectronic CF_2O ^{12,13}. Figure 3 shows the low-temperature infrared spectra of solid $\text{NF}_3\text{O} \cdot x\text{AsF}_5$. The latter spectra were obtained by admitting at 25° an equimolar amount of gaseous NF_3O and AsF_5 at a total pressure of about 4 mm into the cell. Subsequently, cooling of the internal window by liquid nitrogen was started. As soon as the first visible, solid deposit had formed on the internal window, pumping on the sample was started to avoid deposition of unreacted starting materials. The absence of solid AsF_5 in the spectra can be readily established by comparison with the spectrum previously reported¹⁴ for this compound. Below 800 cm^{-1} a remarkable frequency shift and appearance of additional bands was observed in the spectra (shown in Figure 3) when compared to that of Figure 1. Warming up of the sample (deposited on the internal cold window) to about 10° under pumping followed by cooling, resulted in spectra resembling closely to that shown in Figure 1. Low-temperature spectra were also recorded on solid $\text{NF}_3\text{O} \cdot x\text{BF}_3$ samples (see Figure 4). In addition to bands characteristic for NF_2O^+ and B_2F_7^- ^{15,16} those characteristic for solid BF_3 ¹⁷ were always present. Attempts to remove the excess BF_3 resulted in the simultaneous removal of the complex itself. The spectrum of a typical mixture showed absorptions at the following wave-numbers: 1855, m; 1420, s, br; 1340, mw; 1220, m, br; 1165, vs; 1150-950, s, br; 899, ms; 884, w; 836, ms; 735, m, br; 650, m, sh; 630, s, br; 570, m; 551, w; 528, mw; 520, mw; 472, m; and 455, w. Figure 5 shows the Raman spectrum of solid $\text{NF}_2\text{O}^+ \text{AsF}_6^-$. The observed frequencies are listed in Table 1.

- (12) A. H. Nielsen, T. G. Burke, P. J. H. Woltz, and E. A. Jones, J. Chem. Phys., 20, 596 (1952).
- (13) J. Overend and J. C. Evans, Trans. Faraday Soc., 55, 1817 (1959).
- (14) K. O. Christe and A. E. Pavlath, Z. Anorg. Allgem. Chem., 335, 210 (1965).
- (15) S. Brownstein and J. Passivirta, Can. J. Chem., 43, 1645 (1965).
- (16) J. J. Harris, Inorg. Chem., 5, 1627 (1966).
- (17) D. A. Dows, J. Chem. Phys., 31, 1637 (1959).

Table 1

Vibrational Spectra of $\text{NF}_2\text{O}^+\text{AsF}_6^-$ and $\text{NF}_2\text{O}^+\text{SbF}_6^-$ and their AssignmentsCompared with those of CF_2O

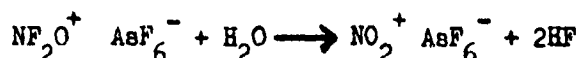
Obsd, freqm cm^{-1}		Assignment (point group)	
CF_2O	$\text{NF}_2\text{O}^+\text{AsF}_6^-$	$\text{NF}_2\text{O}^+\text{SbF}_6^-$	AsF_6^- or SbF_6^-
Infrared	Infrared	Raman	Infrared
			(C_{2v})
3851 w	3706 w		2 ν_2 (A_1)
2195 w	2055 w		$\nu_1 + \nu_4$ (B_1)
1928 ms	1858 ms	1863 (O+)	ν_{asym}, ν_2 (A_1)
1907 w, sh	1791 w		2 ν_1 (A_1)
	1300 w, br		
	1201 w		
1249 vs	1162 s	1169 (O+)	$\nu_{\text{asym}} \text{XF}_2, \nu_4$ (B_1)
	1135 w, sh		2 ν_5 (A_1)
965 s	898 ms	902 (4)	ν_1 (A_1)
	827 w		
774 ms	720 ms, sh		$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)
	692 vs		ν_3 (F_{1u})
		689 (10)	ν_1 (A_{1g})
626 m	645 m	634 (1)	ν_2 (E_g)
		584 (2)	
584 m	569 mw, br	573 (2)	ν_4 (F_{1u})
	392 m		ν_5 (F_{2g})
		373 (2)	

DISCUSSION

Synthesis and Properties

The preparation of $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ presents no difficulties since the two starting materials, NF_3O and AsF_5 , have a common liquid phase. In the case of the corresponding SbF_6^- salt, HF was chosen as a solvent owing to the low boiling point (-85°) of NF_3O^2 and high melting point (7°) of SbF_5 . In this manner NF_3O can always be kept in excess and the formation of undesirable polymeric anions,^{18,19} such as $\text{Sb}_2\text{F}_{11}^-$, can be avoided. For the synthesis of $\text{NF}_2\text{O}^+ \text{B}_2\text{F}_7^-$ the use of excess NF_3O is advisable, since excess NF_3O can be removed from the solid adduct more easily than excess BF_3 . The fact that only the 1:2 adduct is formed at -126° , even if a large excess of NF_3O is used in its preparation, is unexpected, since at -95° the 1:1 adduct is more stable than the 1:2 adduct. The preferred formation of the 1:2 adduct might be explained assuming that its formation is kinetically favored over that of the 1:1 adduct.

The NF_3O - Lewis acid adducts are white, crystalline hygroscopic solids. Their thermal stability decreases with decreasing strength of the Lewis acid. The SbF_5 and the AsF_5 salt are quite stable and have been stored in a Teflon FEP container for several months without noticeable decomposition. They act as oxidizers and react violently with water. With a limited amount of water partial hydrolysis takes place according to:



The heat of dissociation⁸, $17.80 \text{ kcal mole}^{-1}$, obtained for $\text{NF}_2\text{O}^+ \text{BF}_4^-$ is of the same order of magnitude as the values obtained for similar ionic complexes such as $\text{ClF}_2^+ \text{BF}_4^-$ ²⁰ ($23.6 \text{ kcal mole}^{-1}$) and $\text{NO}^+ \text{ClF}_2^-$ ²¹ ($15.5 \text{ kcal mole}^{-1}$). Unfortunately, only an estimated value⁹ was available for the heat of formation of NF_3O . Therefore, the ΔH_{f298}° value of $\text{NF}_2\text{O}^+ \text{BF}_4^-$ contains the possible error

(18) J.K. Ruff, *Inorg. Chem.*, **5**, 1791 (1966).

(19) J. Weidlein and K. Dehnicke, *Z. Anorg. Allgem. Chem.*, **348**, 278 (1966).

(20) H. Selig and J. Shamir, *Inorg. Chem.*, **3**, 294 (1964).

(21) K.O. Christe and J.P. Guertin, *ibid.*, **4**, 905 (1965).

inherent in the estimated value of ΔH_f^0 of $\text{NF}_3\text{O}(g)$ used in our calculation.

Vibrational Spectra

The 1:1 adducts between NF_3O and Lewis acids could be either fluorine or oxygen bridged coordination complexes or be ionic. The simplicity of the observed infrared spectra, the occurrence of the bands characteristic for AsF_6^- and SbF_6^- , and the strong frequency shift of the N-O stretching vibration (when compared to free NF_3O) to higher wavenumbers suggest that the 1:1 adducts are ionic. Consequently, the NF_3O part of the adduct should be present in the form of NF_2O^+ . Table 1 lists the observed frequencies for $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ and $\text{NF}_2\text{O}^+ \text{SbF}_6^-$ together with their assignment. The vibrations belonging to AsF_6^- and SbF_6^- will be discussed first, since they can be assigned more easily by comparison with similar complexes containing these anions. An octahedral anion of the type XF_6^- has O_h symmetry. The six normal modes of vibration are classified as ($A_{1g} + E_g + 2F_{1u} + F_{2u}$). Of these, only the two F_{1u} modes will be infrared active, while only the A_{1g} , E_g , and F_{2g} modes will be Raman active, provided that the selection rules are valid and that the octahedron is not distorted. The remaining F_{2u} mode is inactive in both the infrared and Raman spectrum. By comparison with the vibrational spectra of $\text{K}^+ \text{AsF}_6^-$, $\text{NF}_4^+ \text{AsF}_6^-$, $\text{ClF}_2^+ \text{AsF}_6^-$, $\text{Na}^+ \text{SbF}_6^-$, $\text{Li}^+ \text{SbF}_6^-$, and $\text{ClF}_4^+ \text{SbF}_6^-$, the normal modes belong to AsF_6^- and SbF_6^- , respectively, can be assigned without difficulty, the observed frequencies and intensities being in good agreement.

The remaining bands observed in the spectra of both, $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ and $\text{NF}_2\text{O}^+ \text{SbF}_6^-$, complexes should be due to the NF_2O^+ cation. This cation is isoelectronic with CF_2O and, hence, can be expected to have a similar structure. Comparison

- (22) K. Bühler, Dissertation, Technische Hochschule, Stuttgart, Germany, (1959).
- (23) K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, *Inorg. Chem.*, **6**, 533 (1967).
- (24) K. O. Christe and W. Sawodny, *ibid.*, **6**, 513 (1967).
- (25) W. Sawodny, unpublished results.
- (26) G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, **6**, 2212 (1967).
- (27) K. O. Christe and W. Sawodny, to be published.

of the spectra of NF_2O^+ with that previously reported^{12,13} for CF_2O (see Table I) shows that both the frequencies and relative intensities are very similar. Therefore, the assignments for NF_2O^+ were made for point group C_{2v} . All six fundamentals (classified as $3\text{A}_1 + 2\text{B}_1 + \text{B}_2$) should be infrared and Raman active and in analogy to those of CF_2O . The fact that $\nu_6^- (\text{B}_2)$ was not observed in the Raman spectrum is not surprising and is due to its low relative intensity. In planar XY_3 the corresponding out of plane deformation mode is Raman inactive.

The low-temperature infrared spectrum of $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ (see Figure 3) shows practically no frequency shift for ν_1, ν_2, ν_3 , and ν_4 of NF_2O^+ when compared to that obtained for the complex as a dry powder at 25° (see Figure 1). The bands at 664 and 729 cm^{-1} in the low-temperature spectrum agrees reasonably well with the values assigned to ν_5 and ν_6 , respectively, of NF_2O^+ in the dry powder spectrum (see Table I). However, the band, characteristic for $\nu_3 (\text{F}_{lu})$ of AsF_6^- has a relatively low intensity in the low-temperature spectrum. Hence, it seems likely that the additional bands observed in the range 600 to 770 cm^{-1} and possibly also the band at 491 cm^{-1} , are As-F vibrations and belong to polymeric anions, such as $\text{As}_2\text{F}_{11}^-$. This assignment is supported by the fact that warming of the sample (deposited on the cold window) close to ambient under pumping, followed by cooling, resulted in a spectrum resembling closely to that of Figure 1. Similarly, in the low-temperature infrared spectrum of the $\text{NF}_3\text{O} \cdot x\text{BF}_3$ complex the bands characteristic for NF_2O^+ ($1855 (\nu_2)$, $1165 (\nu_4)$, $899 (\nu_1)$, $735 (\nu_6)$, $650 (\nu_5)$, and $570 \text{ cm}^{-1} (\nu_3)$) were present in addition to those characteristic for B_2F_7^- ^{15,16} (1220 , 1150 – 950 , and 836 cm^{-1}). The remaining bands can be assigned to solid BF_3 ¹⁷ (1420 , 1340 , 630 , and 472 cm^{-1}). Attempts to remove the solid BF_3 from the cold AgCl window without removing the complex itself were unsuccessful owing to the difficulties to control and maintain the temperature of the cold window closely. This is not surprising since in the synthesis of $\text{NF}_2\text{O}^+ \text{B}_2\text{F}_7^-$ (see above) the same difficulty was encountered. Other structures, theoretically possible for a 1:2 complex between NF_3O and BF_3 , such as $[\text{BF}_3 \leftarrow \text{ONF}_2]^+ [\text{BF}_4]^-$ (NF_2O^+ being isoelectronic with CF_2O might be expected to exhibit donor properties towards Lewis acids similar to those of

(28) J. Goubeau and W. Bues, Z. Anorg. Allgem. Chem., **268**, 221 (1952).

(29) N.N. Greenwood, J. Chem. Soc., 3811 (1959).

(30) J.A.A. Ketelaar and R.L. Fulton, Z. Elektrochem., **64**, 641 (1960).

a carbonyl group ³¹⁾ can be ruled out based on the spectra. For a structure such as $[\text{BF}_3 \leftarrow \text{ONF}_2]^+ [\text{BF}_4]^-$ one would expect to observe the bands characteristic for BF_4^- ^{24,28-30} and a strong frequency decrease of the N=O stretching vibration when compared to the free NF_2O^+ cation.

The infrared data reported in this paper agree well with those previously reported for some of the bands of $\text{NF}_2\text{O}^+ \text{SbF}_6^-$ ⁴ and $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ ^{4,5}. Furthermore, they confirm the ionic structures previously suggested ^{4,5} for these adducts.

Assignment of the four bands in the spectrum obtained for the hydrolysis product of $\text{NF}_2\text{O}^+ \text{AsF}_6^-$ presents no difficulties. The bands at 697 and 400 cm^{-1} are assigned to $\gamma_3 (F_{lu})$ and $\gamma_4 (F_{lu})$, respectively, of AsF_6^- , whereas the bands at 2360 and 598 cm^{-1} are characteristic for $\gamma_3 (\Sigma u^+)$ and $\gamma_2 (\pi u)$, respectively, of NO_2^+ ^{32,33}.

In summary, the vibrational spectra of the 1:1 adducts between NF_3O and Lewis acids are consistent with ionic structures containing the NF_2O^+ cation. All six fundamentals expected for NF_2O^+ were observed with proper frequencies and intensities. The low-temperature spectra are indicative of ionic structures containing the NF_2O^+ cation and dimeric anions.

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- (31) I. Lindquist, "Inorganic Adduct Molecules of Oxo-Compounds," *Anorganische und Allgemeine Chemie in Einzeldarstellungen*, Vol. 4, M. Becke-Goehring, Ed. Academic Press Inc., New York, N.Y., 1963.
- (32) J. C. Evans, H. W. Rinn, S. J. Kuhn and G. A. Olah, *Inorg. Chem.*, **3**, 857 (1964).
- (33) K. O. Christe, unpublished results.

R-7723

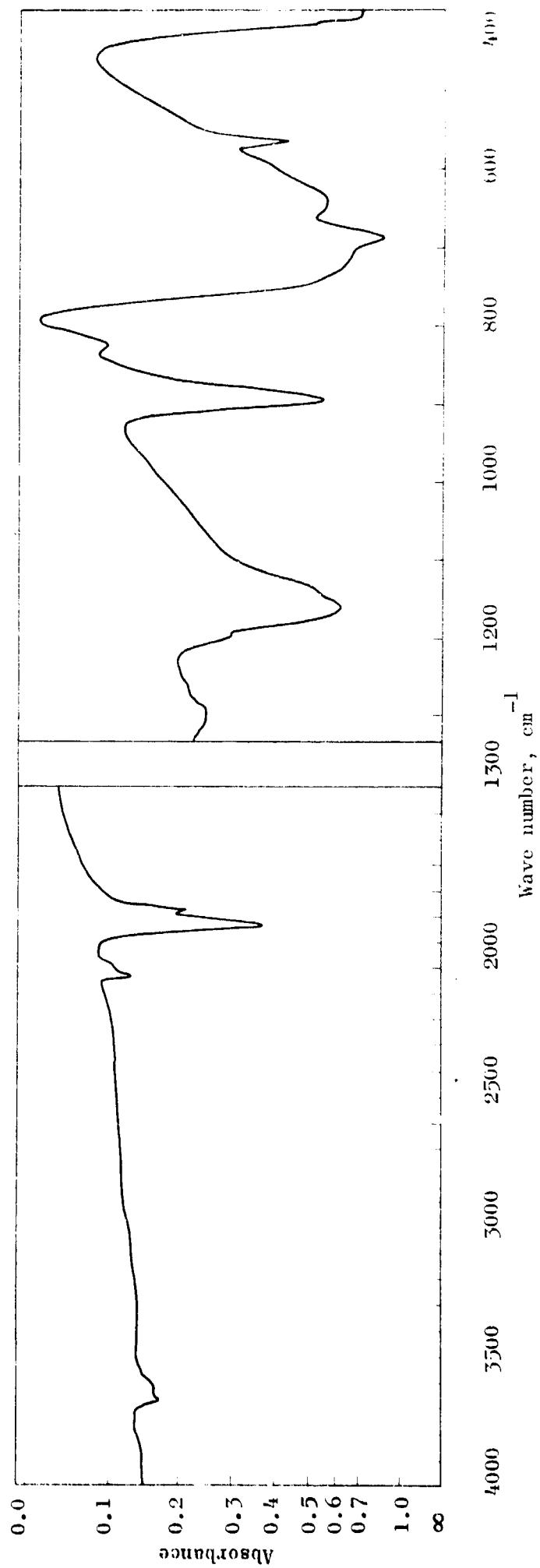


Figure 1. Infrared Spectrum of $\text{Ni}_2\text{O}^+ \text{AsF}_6^-$ as Dry Powder

A-15

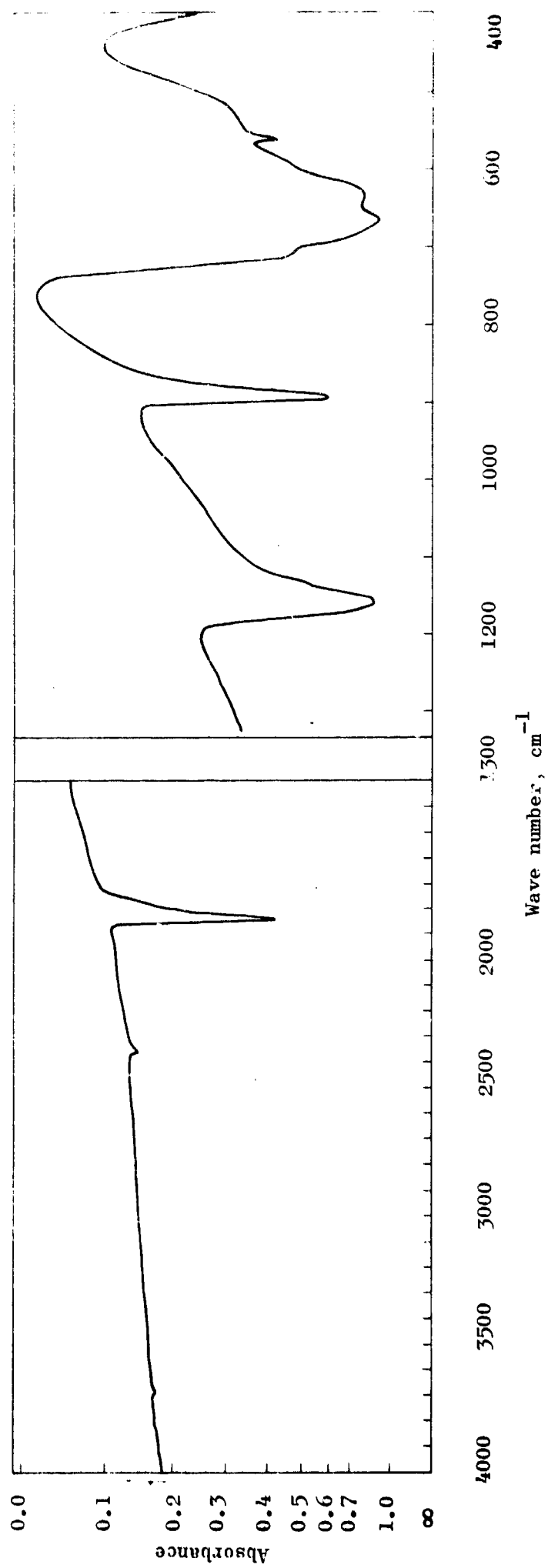


Figure 2. Infrared Spectrum of $\text{NF}_2\text{O}^+ \text{SbF}_6^-$ as Dry Powder

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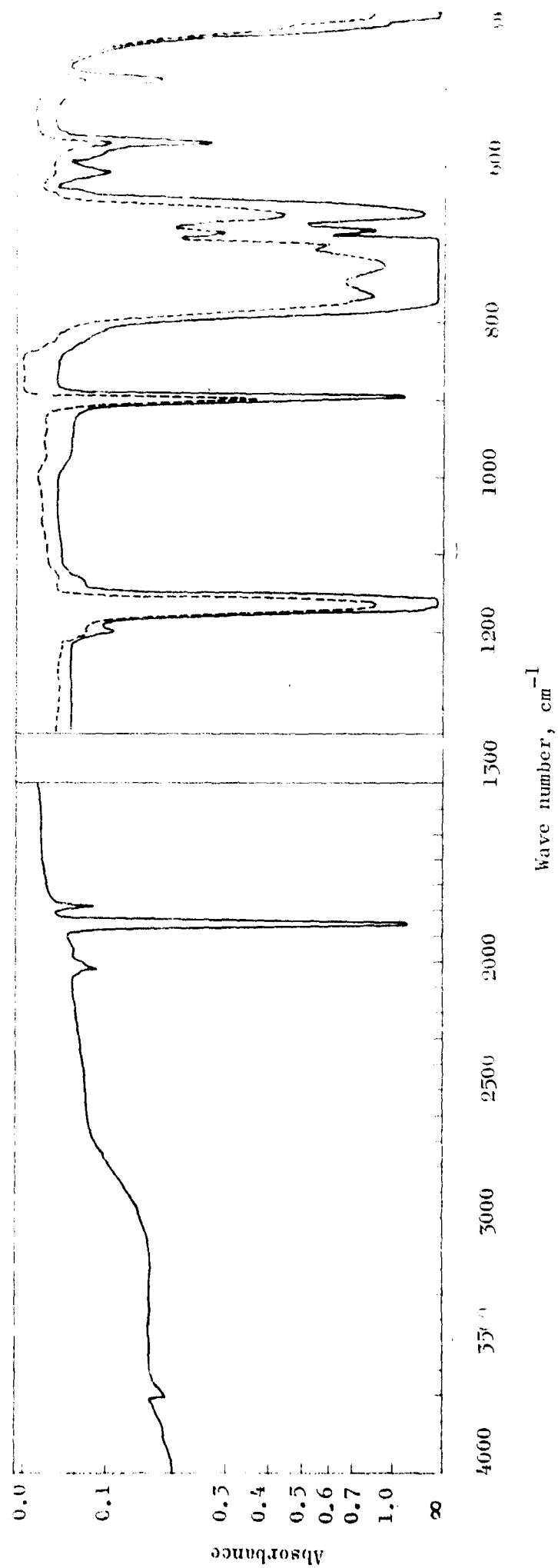


Figure 3. Low-Temperature Infrared Spectrum of NF_5OAsF_5 at Two Different Concentrations

A-17

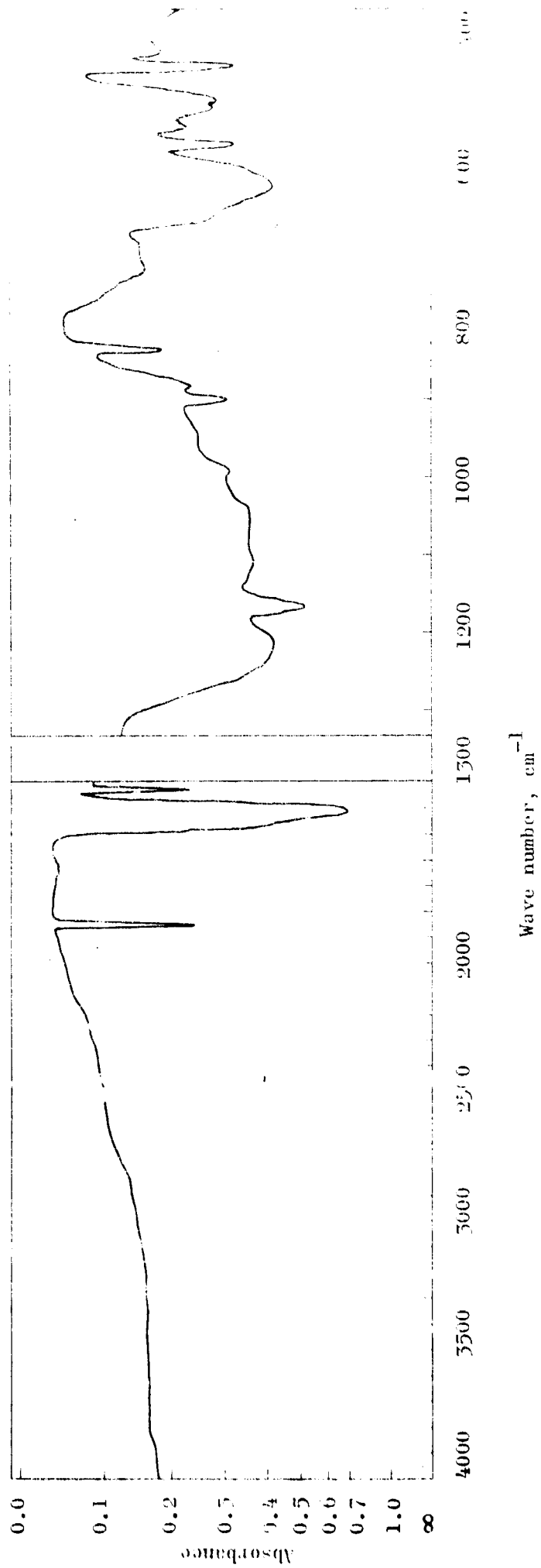


Figure 4. Low-Temperature Infrared Spectrum of $\text{NF}_3\text{O} \cdot x\text{BF}_3$

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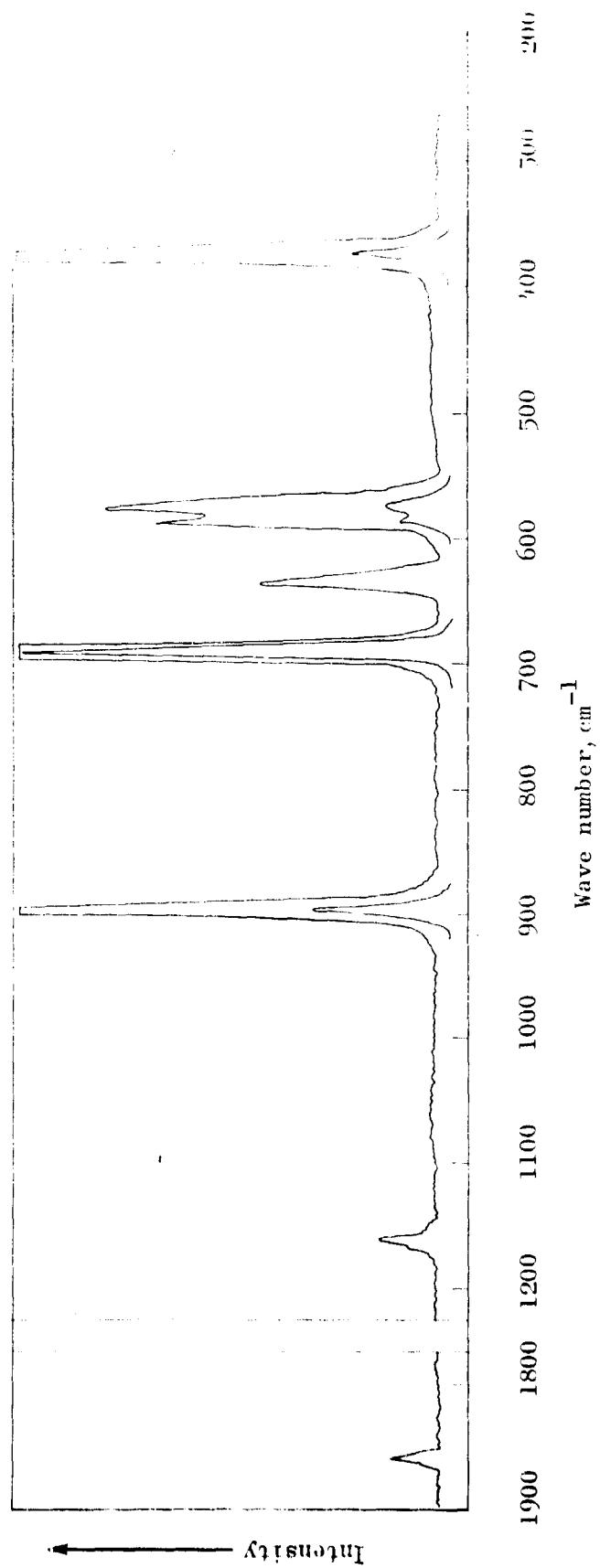


Figure 5. Raman Spectrum of Solid $\text{NF}_2\text{O}^+\text{AsF}_6^-$

A-19/A-20

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Security Classification

DOCUMENT CONTROL DATA - R & D

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13. ABSTRACT New species such as ClF_5O , ClF_5O_2 , and BrF_7 were sought via glow discharge fluorination with suitable substrates. These techniques, as well as the high pressure-temperature fluorination of $\text{ClF}_2\text{OAsF}_6$ and ClO_2AsF_6 , were unsuccessful. The high-pressure fluorination technique also failed to give OF_3^+ , AnF^+ , ClF_6^+ , and BrF_6^+ salts. A complete structural investigation of ClF_5O , ClF_4O^- , ClF_5O^+ , and ClO_2^+ showed symmetries of these ions to be C_s , C_{4v} , C_s , and C_{2v} , respectively. In addition, dissociation pressure data for ClO_2BF_4 was measured permitting an assignment of relative base strength to chlorine fluorides. Pure FIO_2 has been prepared and its salts with Lewis acids are being studied. A new synthesis of SOF_4 was uncovered through the action of ClF on thionyl fluoride. (C)			

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14	REMARKS	UNEP A		UNEP B		UNEP C	
		ROLE	WT	ROLE	WT	ROLE	WT
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